Quality Assurance Project Plan Addendum 1
(Revision 1 – May 2009)

U.S. Coast Guard Old Station Ludington
Ludington, Michigan

May 2009

Prepare

ARCAD

28550 C
Suite 50
Novi, M
48377
(248) 99

Prepared for

U.S. Coast Guard

U.S. Department of Homeland Security

United States Coast Guard

Commanding Officer
United States Coast Guard
Civil Engineering Unit Cleveland

1240 East Ninth Street
Room 2179
Cleveland Ohio 44199-2060
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11000
JUN 15 2009

U.S. Environmental Protection Agency
Region 5
Mr. Owen Thompson
Remedial Project Manager
Superfund Division
77 West Jackson Blvd.
Mail Code SR-6J
Chicago, IL 60604

Dear Mr. Thompson:

Attached for your records as enclosure (1) is the Quality Assurance Project Plan (QAPP) Addendum 1, Revision 1 - May 2009 for the investigation at the U.S. Coast Guard Old Station Ludington located in Mason County, Ludington, Michigan.

If you have any comments to this document, please contact Mr. Greg Carpenter at 216-902-6219.

Sincerely,

Frank A. Blaha
Chief, Environmental Compliance
By direction of the Commanding Officer

Enclosures: (1) U.S. Coast Guard Quality Assurance Project Plan Addendum 1, Revision 1 May 2009 Old Station Ludington, Ludington, Michigan.

OWEN
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06/30/2009 03:53 PM

To Frank A. Blaha
cc Gregory O. Carpenter, Michael Chrystof/R5/USEPA/US
bcc

Subject Fw: Scan from a Xerox WorkCentre

Frank-

EPA has completed its review of the QAPP Addendum 1, (Rev. 1 - May 2009) USCG Old Station Ludington, transitted by your June 15, 2009 letter.

The QAPP revision is acceptable and EPA has no comments.

We have signed the appropriate boxes on Worksheet 3 and the pdf is provided below.

If you need anything in addition in writing please let me know.

W. Owen Thompson
Remedial Project Manager
Superfund Remedial Response Section Six
U.S. EPA Region 5, SR-6J
77 W. Jackson Blvd.
Chicago, IL 60604
Phone (312) 886-4843
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ARCADIS

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ENVIRONMENT

Gregory Carpenter
U.S. Coast Guard
Civil Engineering Unit Cleveland
1240 East Ninth Street
Cleveland, OH 44199-2060

Subject:
Quality Assurance Project Plan (QAPP) Addendum 1, (Revision 1 - May 2009)
U.S. Coast Guard Old Station Ludington, Ludington, Michigan

Date:
May 26, 2009

Contact:
Troy Sclafani

Phone:
248.994.2252

Email:
Troy.Sclafani@arcadis-us.com

Project Number:
DE000122.0001

Dear Greg:

TestAmerica has discontinued the use of laboratory analytical equipment necessary to perform analysis of metals by atomic adsorption spectrophotometry using U.S. Environmental Protection Agency (USEPA) Method 7420. ARCADIS and TestAmerica recommend using USEPA Method 6010B for analysis of soil and 6020A for analysis of water (e.g., blanks and groundwater samples) during future project activities for the above-referenced site. Therefore, as indicated in the recently finalized Removal Action Work Plan (RAWP), ARCADIS has prepared and enclosed Quality Assurance Project Plan (QAPP) Addendum Number 1. The QAPP Addendum Number 1 consists of:

- revisions to select worksheets within the QAPP to document the new analytical methods (6010B and 6020A);
- revisions to select worksheets within the QAPP to include specific references to the RAWP; and
- addition of associated laboratory standard operating procedures (SOPs) for USEPA methods 6010B and 6020A.

A summary of affected worksheets and the associated revisions is provided in Table 1 (attached). If the revisions are acceptable to the USCG, then ARCADIS recommends that the USCG obtain signatures from project personnel acknowledging their acceptance of QAPP Addendum Number 1. The acknowledgement signatures should be obtained from all project personnel listed on the project distribution list and documented on revised Worksheet #3. All copies of the QAPP should be updated with the revised worksheets (Revision 1 April 2009) and associated laboratory SOPs.

If you have any questions, please feel free to call Rob Ellis at 248.994.2252 or Dennis Capria at 315.671.9299.

Sincerely,

ARCADIS

Troy Sclafani
Project Scientist/Associate Project Manager

Dennis K. Capria

Dennis Capria
Principal Scientist/Data Quality Assurance Manager

Attachments:
Table 1 - Summary of Revisions to Worksheets
Revised QAPP Worksheets (Revision 1)
Laboratory Analytical SOPs (ICP and ICP-MS)

Copies:
Mr. Frank Blaha – USCG CEU Cleveland
Mr. Owen Thompson – USEPA Region 5
Mr. Mike Chrystof – USEPA Region 5
Mr. Warren Topel – TestAmerica
Mr. Paul Junio – TestAmerica
Mr. Greg Zelmer – ARCADIS
Mr. Rob Ellis – ARCADIS

TABLES

Table 1. Summary of Revisions to Worksheets within the QAPP (Revision 1 – May 2009) for USCG Old Station Ludington, Ludington, Michigan.

Work Sheet Numbers	Revision Number	Revision Date	Description of Revisions
1, 4-10,13-14, 16, 22, 26-27, 29-35	None	None	Not Applicable
2, 3, 11, 12, 17-21, 28	1	April 2009	Added reference to RAWP, where applicable
18, 20	1	April 2009	Added row for removal action confirmation sample details
12-1, 12-2, 15-1, 15-2, 23-25, 36	1	April 2009	• Revised to incorporate USEPA Method 6010B and/or 6020A and reference to associated laboratory analytical SOPs for ICP and ICP-MS, where applicable • Incorporated reporting limits associated with Methods 6010B and/or 6020, where applicable • Incorporated measurement performance criteria associated with Methods 6010B and/or 6020A, where applicable • Revised QA/QC acceptance criteria and evaluation limits, where applicable

WORKSHEETS

QAPP Worksheet #2 QAPP Identifying Information

Site Name/Project Name:	U.S. Coast Guard Old Station Ludington
Site Location:	The Old Station Ludington is located at 101 South Lakeshore Drive in the City of Ludington, in Mason County, Michigan. The site is situated in Section 16, Township 18 North (T18N), and Range 18 West (R18W) in Michigan.
Site Number/Code:	NA
Operable Unit:	NA
Contractor Name:	NA
Contractor Number:	NA
Contract Title:	NA
Work Assignment Number:	NA
Identify guidance used to prepare QAPP:	Uniform Federal Policy for Quality Assurance Project Plans, Manual VI (2005)
Identify regulatory program:	Comprehensive Environmental Response, Compensation and Liability Act (CERCLA)
Identify approval entity:	NA
Indicate whether the QAPP is a generic or a project-specific QAPP?	This QAPP is a project-specific QAPP intended to serve the needs of the Site Evaluation and Removal Action activities as described in the FSP (ARCADIS G&M of Michigan, LLC 2008) and the RAWP (ARCADIS G&M of Michigan, LLC 2009).
List dates of scoping sessions that were held:	June 20, 2007 at USEPA Region 5 offices in Chicago, Illinois

QAPP Worksheet #2 QAPP Identifying Information

List dates and titles of QAPP documents written for previous site work, if applicable:	
Quality Assurance Project Plan	NA
List organizational partners (stakeholders) and connection with lead organization:	U.S. Coast Guard – Lead Agency
List data users:	U.S. Coast Guard Project Team
Lead Organization's Program Manager:	Frank Blaha, U.S. Coast Guard, Program Manager

QAPP Worksheet #2 QAPP Identifying Information

Required QAPP Element(s) and Corresponding QAPP Section(s) (per UFP QAPP 2005)	Required Information	Crosswalk to Related Information and Documents
Project Management and Objectives		
2.1 Title and Approval Page	- Title and Approval Page	– Worksheet #1 Title and Approval Page
2.2 Document Format and Table of Contents 2.2.1 Document Control Format 2.2.2 Document Control Numbering System 2.2.3 Table of Contents 2.2.4 QAPP Identifying Information	- Table of Contents - QAPP Identifying Information	– The Table of Contents is provided following the QAPP cover page. – Worksheet #2 QAPP Identifying Information
2.3 Distribution List and Project Personnel Sign-Off Sheet 2.3.1 Distribution List 2.3.2 Project Personnel Sign-Off Sheet	- Distribution List - Project Personnel Sign-Off Sheet	– Worksheet #3 Distribution List/ Personnel Sign-Off Note: Worksheet 3 and 4 combined

QAPP Worksheet #2 QAPP Identifying Information

Required QAPP Element(s) and Corresponding QAPP Section(s) (per UFP QAPP 2005)	Required Information	Crosswalk to Related Information and Documents
2.4 Project Organization 2.4.1 Project Organizational Chart 2.4.2 Communication Pathways 2.4.3 Personnel Responsibilities and Qualifications 2.4.4 Special Training Requirements and Certification	- Project Organizational Chart - Communication Pathways - Personnel Responsibilities and Qualifications Table - Special Personnel Training Requirements Table	– Worksheet #5 Project Organization Chart – Worksheet #6 Communication Pathways – Worksheet #7 Personnel Responsibilities and Qualifications and – Worksheet #8 Special Personnel Training Requirements
2.5 Project Planning/Problem Definition 2.5.1 Project Planning (Scoping) 2.5.2 Problem Definition, Site History and Background	- Project Planning Session Documentation (including Data Needs tables) - Project Scoping Session Participants Sheet - Problem Definition, Site History and Background - Site Maps (historical and present)	– Worksheet #9 Project Team Planning Sessions Participants' Sheet and – Worksheet #10 Problem Definition for Project Data Quality Objectives) Site history and more detail concerning the project Data Quality Objectives can be found in the Final Phase I Environmental Site Assessment, USCG Station Ludington, Michigan (URS, February 2001), Phase I Environmental Assessment prepared for the City of Ludington (Otwell Mawby, P.C., April 2007), and the FSP (ARCADIS G&M of Michigan, LLC 2008). Site maps are provided in the FSP (ARCADIS G&M of Michigan, LLC 2008) and the RAWP (ARCADIS G&M of Michigan, LLC 2009) prepared for the Site.

QAPP Worksheet #2 QAPP Identifying Information

Required QAPP Element(s) and Corresponding QAPP Section(s) (per UFP QAPP 2005)	Required Information	Crosswalk to Related Information and Documents
2.6 Project Quality Objectives and Measurement Performance Criteria 2.6.1 Development of Project Quality Objectives Using the Systematic Planning Process 2.6.2 Measurement Performance Criteria	- Site-Specific Project Quality Objectives - Measurement Performance Criteria Table	– Worksheet #11 Project Quality Objectives/Systematic Planning Process Statements and – Worksheet #12 Measurement Performance Criteria for project analytes
2.7 Secondary Data Evaluation	- Sources of Secondary Data and Information - Secondary Data Criteria and Limitations Table	– Worksheet #13 Secondary Data Criteria and Limitations
2.8 Project Overview and Schedule 2.8.1 Project Overview 2.8.2 Project Schedule	- Summary of Project Tasks - Reference Limits and Evaluation Table - Project Schedule/Timeline Table	– Worksheet #14 Summary of Project Tasks – Worksheet #15 Reference Limits and Evaluation for specific monitoring activities and – Worksheet #16 Project Schedule/Timeline

QAPP Worksheet #2 QAPP Identifying Information

Required QAPP Element(s) and Corresponding QAPP Section(s) (per UFP QAPP 2005)	Required Information	Crosswalk to Related Information and Documents
Measurement/Data Acquisition		
3.1 Sampling Tasks		
3.1.1 Sampling Process Design and Rationale	- Sampling Design and Rationale	– Worksheet #17 Sampling Design and Rationale
3.1.2 Sampling Procedures and Requirements	- Sample Location Map	– Worksheet #18 Sampling Locations and Methods/Standard Operating Procedure Requirements for the project
3.1.2.1 Sampling Collection Procedures	- Sampling Locations and Methods/Standard Operating Procedure Requirements Table	– Worksheet #18 Sampling Locations and Methods/Standard Operating Procedure Requirements for the project
3.1.2.2 Sample Containers, Volume and Preservation	- Analytical Methods/Standard Operating Procedure Requirements Table	– Worksheet #19 Analytical Standard Operating Procedure Requirements (Sample Containers Preservation and Holding Times)
3.1.2.3 Equipment/Sample Containers Cleaning and Decontamination Procedures	- Field Quality Control Sample Summary Table	– Worksheet #20 Sample Quantities and Control Frequencies
3.1.2.4 Field Equipment Calibration, Maintenance, Testing and Inspection Procedures	- Sampling Standard Operating Procedures	– Worksheet #21 Field Sampling Standard Operating Procedure References
3.1.2.5 Supply Inspection and Acceptance Procedures	- Field Equipment Calibration, Maintenance, Testing and Inspection Table	– Worksheet #22 Field Equipment Calibration, Maintenance, Testing, and Inspection
3.1.2.6 Field Documentation Procedures		More details concerning the sampling design, rational and procedures can be found in the FSP (ARCADIS G&M of Michigan, LLC 2008) and the RAWP (ARCADIS G&M of Michigan, LLC 2009) prepared for the Site.

QAPP Worksheet #2 QAPP Identifying Information

Required QAPP Element(s) and Corresponding QAPP Section(s) (per UFP QAPP 2005)	Required Information	Crosswalk to Related Information and Documents
3.2 Analytical Tasks 3.2.1 Analytical SOPs 3.2.2 Analytical Instrument Calibration Procedures 3.2.3 Analytical Instrument and Equipment Maintenance, Testing and Inspection Procedures 3.2.4 Analytical Supply Inspection and Acceptance Procedures	- Analytical Standard Operating Procedures - Analytical Standard Operating Procedure References Table - Analytical Instrument Calibration Table - Analytical Instrument and Equipment Maintenance, Testing and Inspection Table	– Worksheet #23 Analytical Standard Operating Procedure References – Worksheet #24 Analytical Instrument Calibration – Worksheet #25 Analytical Instrument and Equipment Maintenance, Testing and Inspection The analytical Standard Operating Procedures can be found in Attachment T-1.
3.3 Sample Collection Documentation, Handling, Tracking and Custody Procedures 3.3.1 Sample Collection Documentation 3.3.2 Sample Handling and Tracking System 3.3.3 Sample Custody	- Sample Collection Documentation Handling, Tracking and Custody Standard Operating Procedures - Sample Container Identification - Sample Handling Flow Diagram - Example Chain-of-Custody Form and Seal	– Worksheet #26 Sample Handling System – Worksheet #27 Sample Custody Requirements – An example of the Chain-of-Custody form can be found in Attachment 1 More details concerning the field sampling procedures can be found in the FSP (ARCADIS G&M of Michigan, LLC 2008) and RAWP (ARCADIS G&M of Michigan, LLC 2009) prepared for the Site.

QAPP Worksheet #2 QAPP Identifying Information

Required QAPP Element(s) and Corresponding QAPP Section(s) (per UFP QAPP 2005)	Required Information	Crosswalk to Related Information and Documents
3.4 Quality Control Samples 3.4.1 Sampling Quality Control Samples 3.4.2 Analytical Quality Control Samples	- QC Samples Table - Screening/Confirmatory Analysis Decision Tree	– Worksheet #28 presents Quality Control sample information for project analytes
3.5 Data Management Tasks 3.5.1 Project Documentation and Records 3.5.2 Data Package Deliverables 3.5.3 Data Reporting Formats 3.5.4 Data Handling and Management 3.5.5 Data Tracking and Control	- Project Documents and Records Table - Analytical Services Table	– Worksheet #29 Project Documents and Records – Worksheet #30 Analytical Services

QAPP Worksheet #2 QAPP Identifying Information

Required QAPP Element(s) and Corresponding QAPP Section(s) (per UFP QAPP 2005)	Required Information	Crosswalk to Related Information and Documents
Assessment/Oversight		
4.1 Assessments and Response Actions 4.1.1 Planned Assessments 4.1.2 Assessment Findings and Corrective Action Responses	- Assessments and Response Actions - Planned Project Assessments Table - Audit Checklists - Assessment Findings and Corrective Action Responses Table	- Worksheet #31 Planned Project Assessments - Worksheet #32 Assessment Findings and Corrective Action Responses Laboratory Certifications can be found in Attachment 2
4.2 QA Management Reports	- Conformance of project activities to QAPP requirements and procedures - Status of project and schedule delays - Deviations from the approved QAPP and approved amendments to the QAPP - Results of data review activities - Required corrective actions and effectiveness of corrective action implementation - Data usability assessments in terms of precision, accuracy, representativeness, completeness, comparability, and sensitivity	- Worksheet #33 Quality Assurance Management Reports
4.3 Final Project Report	- All Quality Assurance Management Reports attached - Additional data quality concerns and resolution documentation	- Worksheet #33 Quality Assurance Management Reports

QAPP Worksheet #2 QAPP Identifying Information

Required QAPP Element(s) and Corresponding QAPP Section(s) (per UFP QAPP 2005)	Required Information	Crosswalk to Related Information and Documents
Data Review		
5.1 Overview		
5.2 Data Review Steps 5.2.1 Step I: Verification 5.2.2 Step II: Validation 5.2.2.1 Step IIa Validation Activities 5.2.2.2 Step IIb Validation Activities 5.2.3 Step III: Usability Assessment 5.2.3.1 Data Limitations and Actions from Usability Assessment 5.2.3.2 Activities	- Verification (Step I) Process Table - Validation (Steps IIa and IIb) Process Table - Validation (Steps IIa and IIb) Summary Table - Usability Assessment	– Worksheet #34 Verification (Step I) Process – Worksheet #35 Validation (Steps IIa and IIb) Process – Worksheet #36 Validation (Steps IIa and IIb) Summary – Worksheet #37 Usability Assessment

QAPP Worksheet #2 QAPP Identifying Information

Required QAPP Element(s) and Corresponding QAPP Section(s) (per UFP QAPP 2005)	Required Information	Crosswalk to Related Information and Documents
5.3 Streamlining Data Review 5.3.1 Data Review Steps To Be Streamlined 5.3.2 Criteria for Streamlining Data Review 5.3.3 Amounts and Types of Data Appropriate for Streamlining	None	NA

QAPP Worksheet #3 Distribution List/Project Personnel Sign-Off

QAPP Recipients	Title	Organization	Telephone Number	Fax Number	E-mail Address	Signature/Date QAPP Revision 1 Read	Document Control Number
Frank Blaha	Program Manager	USCG	216.902.6255	216.902.6277	Frank.A.Blaha@uscg.mil		USCG OSL-01
Greg Carpenter	Project Manager	USCG	216.902.6219	216.902.6277	Gregory.O.Carpenter@uscg.mil		USCG OSL-01
Owen Thompson	USEPA Remedial Project Manager	USEPA (Region 5)	312.886.4843	312.353.8426	thompson.owen@epa.gov	W. Owen Thompson 6/30/09	USCG OSL-01
Mike Chrystof	QAPP Reviewer	USEPA (Region 5)	312-353-3705	312.353.8426	chrystof.michael@ epamail.epa.gov	[illegible] 6/30/2009	USCG OSL-01
Greg Zellmer	Project Coordinator	ARCADIS	248.994.2283	248.994.2241	Gregory.Zellmer@arcadis-us.com	[illegible]	USCG OSL-01
Dennis Capria	Data Quality Assurance Manager	ARCADIS	315.671.9299	315.446.7485	Dennis.Capria@arcadis-us.com	Dennis K. Capria	USCG OSL-01
Warren Topel	Laboratory Project Manager	TestAmerica Analytical Testing Corporation	800.833.7036	920.261.8120	Warren.Topel@Testamericainc.c om	Warren Topel 05-12-09	USCG OSL-01
Paul Junio	Laboratory Quality Assurance Manager	TestAmerica Analytical Testing Corporation	800.833.7036	920.261.8120	Paul.Junio@Testamericainc.com	[illegible] 05/12/09	USCG OSL-01

Note: Copies of the QAPP will be distributed to the individuals above. The copies will consist of the following documents: QAPP and any subsequent QAPP revisions and addendums.

Worksheets #3 and #4 have been combined. The project personnel sign-off table above documents key project personnel who have read the applicable sections of the QAPP and will perform the tasks as described in the QAPP.

QAPP Worksheet #11 Project Quality Objectives/Systematic Planning Process Statements

Who will use the data?
Project team, their subcontractors, and overseeing agencies will use the data to assess the efficacy of the Site evaluation and removal action and to confirm adherence to the performance standards.
What will the data be used for?
The data will be used to evaluate the nature and extent of soil lead impacts and potential groundwater impacts, and if impacts are present above the applicable land use criteria, the site characterization data will be used to determine if a removal action is warranted. The data will also be used confirm the achievement of soil removal action objectives.
What types of data are needed? (target analytes, analytical groups, field screening, on-site analytical or off-site laboratory techniques, sampling techniques)
Data include site evaluation samples and groundwater samples to determine the extent of soil lead impacts and potential groundwater impacts. A waste characterization sample will also be collected. Removal action confirmation soil samples will also be needed to verify that removal action objectives are met in accordance with the Removal Action Work Plan (RAWP) (ARCADIS G&M of Michigan, LLC 2009). Standard protocols for sample collection and handling, sample preparation, and analytical methods will be followed. Standard operating procedures are provided in this document and in the FSP (ARCADIS G&M of Michigan, LLC 2008) and RAWP (ARCADIS G&M of Michigan, LLC 2009).
How "good" do the data need to be in order to support the environmental decision?
Site characterization data need to facilitate evaluation of the nature and extent of soil lead impacts and potential groundwater impacts at the Site, and determine if removal action will be necessary. Groundwater samples need to allow assessment of whether soil lead impacts could potentially or have already resulted in groundwater impacts that could pose an unacceptable risk to potential receptors. Removal confirmation samples need to facilitate determination of the completeness of the removal action and whether additional soil removal

QAPP Worksheet #11 Project Quality Objectives/Systematic Planning Process Statements

is needed. Waste characterization data are needed to determine if the soils and water generated during the Site evaluation and/or removal action are characteristically hazardous and to determine the proper means of transportation and disposal. Specific requirements for data quality are identified in Worksheet # 37.
How much data are needed? (number of samples for each analytical group, matrix and concentration)
The number of samples and analyses for each media are summarized in Worksheet #20 and described in the FSP (ARCADIS G&M of Michigan, LLC 2008) and RAWP (ARCADIS G&M of Michigan, LLC 2009).
Where, when, and how should the data be collected/generated?
Soil sampling activities will consist of collecting samples for field and laboratory analysis using manual equipment. Groundwater samples will be collected using low-flow purging and sampling techniques with either a peristaltic pump or decontaminated submersible pump. Data include analytical data for lead in soil by the use of field X-ray fluorescence screening and laboratory-based analyses using USEPA Method SW-846 6010B. Groundwater data will be generated by laboratory analysis of lead using USEPA Method SW-846 6020A and hardness using SM 2340B. Waste characterization data will be generated for soils, groundwater and decontamination water generated during Site activities by laboratory analysis of lead and toxicity characteristic leaching procedure (TCLP) lead ignitability, pH, and paint filter test. The specific sampling program is described in FSP (ARCADIS G&M of Michigan, LLC 2008) and RAWP (ARCADIS G&M of Michigan, LLC 2009). Standard protocols for sample collection and handling, sample preparation, and analytical methods will be followed. Standard operating procedures for field sampling are referenced in this document and provided in the FSP (ARCADIS G&M of Michigan, LLC 2008) and RAWP (ARCADIS G&M of Michigan, LLC 2009).
Who will collect and generate the data?
Project team.

QAPP Worksheet #11 Project Quality Objectives/Systematic Planning Process Statements

How will the data be reported?
Site evaluation data will be reported in an Engineering Evaluation/Cost Analysis for the Site. Removal confirmation data will be reported in a Removal Action Completion Report following the soil removal action at the Site.
How will the data be archived?
All data will be archived by USCG CEU Cleveland in their Cleveland, Ohio office.

QAPP Worksheet #12-1 Measurement Performance Criteria – Metals (Soil)

Matrix	Soil
Analytical Group	Metals
Concentration Level	All

Sampling Procedure[1]	Analytical Method/Standard Operating Procedures[2]	Data Quality Indicators	Measurement Performance Criteria	Quality Control Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
FSP (ARCADIS G&M of Michigan, LLC 2008) and RAWP (ARCADIS G&M of Michigan, LLC 2009).	T-2	Precision — Overall	RPD < 100%	Field duplicate	S&A
		Accuracy/Bias Contamination	< RL	Blanks (field, equipment, calibration, prep.)	S&A
		Accuracy/Bias	%R (90-110)	Initial and continuing calibration verification	A
		Precision — lab	Certain metals (%R [80-120] see analytical SOP	Interference check sample (A and AB)	A
		Accuracy/Bias	%R (75-125)	MS	A
		Accuracy/Bias	%R (75-125)	MSD	A
		Precision	%RPD <20	Laboratory Duplicate or MS/MSD	A
		Accuracy/Bias	%R (80-120)	LCS	A

QAPP Worksheet #12-1 Measurement Performance Criteria – Metals (Soil)

Matrix	Soil				
Analytical Group	Metals				
Concentration Level	All				
Sampling Procedure[1]	**Analytical Method/Standard Operating Procedures[2]**	**Data Quality Indicators**	**Measurement Performance Criteria**	**Quality Control Sample and/or Activity Used to Assess Measurement Performance**	**QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)**
		Accuracy/Bias	%R (75-125)	Post-digestion spike	A
		Precision	%D < 10%	Serial dilution[3]	A

Notes:

LCS Laboratory control sample.
MS Matrix spike.
MSD Matrix spike duplicate.
RL Reporting limit.
RPD Relative percent difference.
SOP Standard operating procedure.
%D Percent difference.
%R Percent recovery.

1. Reference number from QAPP Worksheet #21.
2. Reference number from QAPP Worksheet #23.
3. Performed as needed only for analytes with concentration > 50 times the method detection limit.

QAPP Worksheet #12-2 Measurement Performance Criteria – Metals (Groundwater)

Matrix	Groundwater
Analytical Group	Metals
Concentration Level	All

Sampling Procedure[1]	Analytical Method/Standard Operating Procedures[2]	Data Quality Indicators	Measurement Performance Criteria	Quality Control Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
FSP (ARCADIS G&M of Michigan, LLC 2008)	T-3	Precision — Overall	RPD < 50%	Field duplicate	S&A
		Accuracy/Bias Contamination	< RL	Blanks (field, equipment, calibration, prep.)	S&A
		Accuracy/Bias	%R (90-110)	Initial and continuing calibration verification	A
		Precision — lab	Certain metals (%R [80-120] see analytical SOP	Interference check sample (A and AB)	A
		Accuracy/Bias	%R (75-125)	MS	A
		Accuracy/Bias	%R (75-125)	MSD	A
		Precision	%RPD <20	Laboratory Duplicate or MS/MSD	A
		Accuracy/Bias	%R 80-120%	LCS	A

QAPP Worksheet #12-2 Measurement Performance Criteria – Metals (Groundwater)

Matrix	Groundwater				
Analytical Group	Metals				
Concentration Level	All				
Sampling Procedure[1]	**Analytical Method/Standard Operating Procedures[2]**	**Data Quality Indicators**	**Measurement Performance Criteria**	**Quality Control Sample and/or Activity Used to Assess Measurement Performance**	**QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)**
		Accuracy/Bias	%R (75-125)	Post-digestion spike	A
		Precision	%D < 10%	Serial dilution[3]	A

Notes:

LCS Laboratory control sample.
MS Matrix spike.
MSD Matrix spike duplicate.
RL Reporting limit.
RPD Relative percent difference.
SOP Standard operating procedure.
%D Percent difference.
%R Percent recovery.

1. Reference number from QAPP Worksheet #21.
2. Reference number from QAPP Worksheet #23.
3. Performed as needed only for analytes with concentration > 50 times the method detection limit.

QAPP Worksheet #15-1 Reference Limits and Evaluation — (Soil)

Analyte		Performance Standard Soil	Sediment/Soil	
			Laboratory Low Level RL[1]	Laboratory Med. Level RL[1]
Inorganics				
Lead (7439-92-1) (6010B)[2]		400 mg/kg [3]	1.2 mg/kg	--
Waste Management				
TCLP Lead (1311)[2]		5 mg/L [4]	0.1 mg/L	--
Ignitability (1030)[2]		140 °F	NA	NA
Corrosivity (pH) (9045)[2]		2 ≥ pH ≥ 12.5	NA	NA
Paint Filter Liquids (9095)[2]		P/F	NA	NA

Notes:

1	The target reporting limits are based on wet weight. Actual reporting limits will vary based on sample weight and moisture content.
2	USEPA. Office of Solid Waste and Emergency Response. *Test Methods for Evaluating Solid Waste SW-846 3rd ed.* Washington, DC. 1996.
3	Residential land-use category direct contact value.
4	Toxicity characteristic of the hazardous waste criteria.
°F	Degrees Fahrenheit.
mg/kg	Milligrams per kilogram.
mg/L	Milligrams per liter.
NA	Not applicable.
P/F	Pass/fail.
RL	Reporting limit.
TBD	To be determined.

QAPP Worksheet #15-2 Reference Limits and Evaluation — (Groundwater)

Analyte		Performance Standard Groundwater	Groundwater Laboratory Low Level RL
Inorganics			
Lead (7439-92-1) (6020A)[1]		3 µg/L	0.40 µg/L
Hardness (SM 2340 B)		NA	NA
Waste Management			
TCLP Lead (1311)[1]		5 mg/L[2]	0.1 mg/L
Ignitability (1030)[1]		140 °F	NA
Corrosivity (pH) (9045)[1]		$2 \geq pH \geq 12.5$	NA

Notes:

1	USEPA. Office of Solid Waste and Emergency Response. *Test Methods for Evaluating Solid Waste SW-846 3rd ed.* Washington, DC. 1996.
2	Toxicity characteristic of the hazardous waste criteria.
mg/L	Milligrams per liter.
NA	Not applicable.
RL	Reporting limit.
SM	Standard Method.
µg/L	Micrograms per liter.

QAPP Worksheet #17 Sampling Design and Rationale

Describe and provide a rationale for choosing the sampling approach (e.g., grid system, biased statistical approach):

Details of the Site evaluation and removal action confirmatory sampling program are provided in the FSP (ARCADIS G&M of Michigan, LLC 2008) and RAWP (ARCADIS G&M of Michigan, LLC 2009).

Describe the sampling design and rationale in terms of what matrices will be sampled, what analytical groups will be analyzed and at what concentration levels, the sampling locations (including QC, critical, and background samples), the number of samples to be taken, and the sampling frequency (including seasonal considerations) [May refer to map or Worksheet #18 for details]:

Lead in soil will be sampled. The goal is to delineate the nature and extent of impacts above the RAO, remove soils containing lead at concentrations above the RAO, and/or characterize the residual impacts to be left in place. All soil samples submitted for lead analysis will be prepared for fine and coarse fraction analysis. The fine fraction is defined as the portion of soil that passes through a 250-micron (60-mesh) sieve. The coarse fraction is the portion of sample retained by the 250-micron (60-mesh) sieve. The total lead concentration is then calculated based on the weight of each fraction.

Groundwater sampling will be performed by installing and sampling 3 monitoring wells to evaluate the potential for lead impacts in groundwater.

Site evaluation soil samples will be collected to evaluate the nature and extent of soil lead impacts located adjacent to Site structures. Groundwater samples will be collected to evaluate the potential for soil impacts to affect groundwater. The estimated number of samples, including type and frequency of quality control samples, is provided in Worksheet #18 and in the FSP (ARCADIS G&M of Michigan, LLC 2008). Seasonal considerations are not expected to affect site evaluation sampling.

Removal confirmation samples will be collected to verify the successful removal of soil impacted at concentrations above the RAO of 400 mg/kg. The estimated number of samples, including type and frequency of quality control samples, is provided in Worksheet #18, in the FSP (ARCADIS G&M of Michigan, LLC 2008) and the RAWP (ARCADIS G&M of Michigan, LLC 2009). Removal confirmation sampling is expected to be completed in one field event and will therefore not be affected by seasonal considerations.

Waste characterization samples will be collected from soils and groundwater and analyzed for lead, TCLP lead, ignitability, pH and paint filter test.

QAPP Worksheet #18 Sampling Locations and Methods/Standard Operating Procedure Requirements

Sampling Location/Identification Number	Matrix	Sample Type and Number: Depth Intervals	Analytical Group	Concentration Level	Number of Samples (plus field duplicates)[1]	Sampling Standard Operating Procedure Reference Number[2]	Rationale for Sampling Location
Old Station Ludington	Soil	40[A] grab samples: 0 to 6 inches	Metals (Lead only)	Normal	40[A] + 4 field duplicates	FSP (ARCADIS G&M of Michigan, LLC 2008) – Appendix B	Horizontal and vertical delineation of impacts in accordance with the FSP (ARCADIS G&M of Michigan, LLC 2008)
Old Station Ludington	Soil	32[A] grab samples: 0 to 6 inches	Metals (Lead only)	Normal	32[A] + 4 field duplicates	RAWP (ARCADIS G&M of Michigan, LLC 2009) – Appendix B	Removal action confirmation samples in accordance with the RAWP (ARCADIS G&M of Michigan, LLC 2009)
Old Station Ludington	Groundwater	12[A] groundwater samples:	Metals (Lead only) and Hardness (as mg/L CaCO3)	Normal	12[A] + 4 field duplicates	FSP (ARCADIS G&M of Michigan, LLC 2008) – Appendix B	Groundwater evaluation in accordance with the FSP (ARCADIS G&M of Michigan, LLC

QAPP Worksheet #18 Sampling Locations and Methods/Standard Operating Procedure Requirements

Sampling Location/Identification Number	Matrix	Sample Type and Number: Depth Intervals	Analytical Group	Concentration Level	Number of Samples (plus field duplicates)[1]	Sampling Standard Operating Procedure Reference Number[2]	Rationale for Sampling Location
							2008).
Old Station Ludington	Soil and Groundwater	2 (composite) waste characterization samples	Metals (Lead only), TCLP Metals (Lead only), ignitability, pH, and Paint Filter Test	Normal	2	FSP (ARCADIS G&M of Michigan, LLC 2008) – Appendix B	Characterization of waste generated during Site evaluation and/or removal action for disposal in accordance with the FSP (ARCADIS G&M of Michigan, LLC 2008).

Notes:

1 One blind duplicate sample will be collected for every 10 samples.
2 Reference number from QAPP Worksheet #21.
A Number of samples is estimated. Number of samples collected will be determined Site evaluation results and final excavation sizes.

QAPP Worksheet #19 Analytical Standard Operating Procedure Requirements (Sample Containers, Preservation, and Holding Times)

Parameter	Analytical and Preparation Method/SOP Reference	Method	Bottle Type	Preservation	Holding Time
Soil					
Metals (Lead)	SOP WT03-08.1 (USEPA Method 6010B), and SOP WT03-07.0 (USEPA Methods 3010 and 3050 [digestion])	6010B [1]	One 4-oz wide-mouth glass jar	Cool to 4°C±2°C	180 days to analyze
Groundwater					
Metals (Total and Dissolved Lead)	SOP WT-ME-200.8_6020 (USEPA Method 6020A), and SOP WT03-07.0 (USEPA Methods 3010 and 3050 [digestion])	6020A [1]	Two 500ml plastic bottles (one filtered and one unfiltered)	HNO3 to pH<2, Cool to 4°C+2°C	180 days to analyze
Hardness	SOP WT03-03.0 (Standard Method SM 2340 B)	SM 2340 B	One 250ml plastic bottle	HNO3 to pH<2, Cool to 4°C+2°C	180 days to analyze
Waste Characterization					
TCLP Metals (Lead)	SOP WT03-08.1 (USEPA Method 6010B), and USEPA Method 1311 (leaching)	6010B [1]	One 4-oz wide-mouth glass jar	Cool to 4°C±2°C	180 days to TCLP extraction and 180 days to analysis
Ignitability (solids)	SOP WT04-03.0 (USEPA Method 1030)	1030 [1]	One 4-oz wide-mouth glass jar	None required	Analyze as soon as possible
pH (soil and waste)	SOP WT05-03.0 (USEPA Method 9045D)	9045D [1]	One 4-oz wide-mouth glass jar	None required	Analyze as soon as possible
Paint Filter Test	SOP WT06-03.0 (USEPA Method 9095B)	9095B [1]	One 4-oz wide-mouth glass jar	None required	None

Notes:

°C Degrees Celsius.
SM Standard Methods
SOP Standard Operating Procedure.
TCLP Toxicity Characteristic Leaching Procedure.
[1] USEPA. Office of Solid Waste and Emergency Response. *Test Methods for Evaluating Solid Waste SW-846,* 3rd ed. Washington, DC. 1996.

QAPP Worksheet #20 Sample Quantities and Control Frequencies

	Laboratory	Analytical and Preparation Standard Operating Procedure[1]	Estimated Environ. Sample Quantity	Field Quality Control Analyses						Laboratory Quality Control Sample						Total
				Trip Blank		Rinsate Blank		Field Duplicate		Matrix Spike		Matrix Spike Duplicate		Laboratory Duplicate		
				Freq.	No.	Freq.	No.	Freq.	No.	Freq.	No.	Freq.	No.	Freq.	No.	
Soil Sampling																
Metals- Lead (Characterization)	TestAmerica	SOP WT03-08.1, Rev 2,and SOP WT03-07.0	40[A]	NA	--	1/day or 1/ 20, whichever is greater	2	1/10	4	1/20	2	NA	--	1/20	2	50
Metals- Lead (Removal Confirmation)	TestAmerica	SOP WT03-08.1, Rev 2,and SOP WT03-07.0	32[A]	NA	--	1/day or 1/ 20, whichever is greater	2	1/10	4	1/20	2	NA	--	1/20	2	40
Groundwater Sampling																
Metals- Lead	TestAmerica	SOP WT-ME-200.8_6020 (USEPA Method 6020A), and SOP WT03-07.0 (USEPA Methods 3010 and 3050 [digestion])	12[A]	NA	--	1/day or 1/ 20, whichever is greater	1	1/10	2	1/20	1	NA	--	1/20	1	17
Hardness	TestAmerica	SOP WT03-03.0 (Standard Method SM 2340 B)	12[A]	NA	--	1/day or 1/ 20, whichever is greater	1	1/10	2	1/20	1	NA	--	1/20	1	17
Waste Characterization																
Metals- Lead	TestAmerica	SOP WT03-08.1, Rev 2,and SOP WT03-07.0	2[A]	NA	--	NA	--	NA	--	NA	--	NA	--	NA	--	2
TCLP Metals- Lead	TestAmerica	SOP WT03-08.1 (USEPA Method 6010B), and USEPA Method 1311 (leaching)	2[A]	NA	--	NA	--	NA	--	NA	--	NA	--	NA	--	2
Ignitability (solids)	TestAmerica	SOP WT04-03.0 (USEPA Method 1030)	2[A]	NA	--	NA	--	NA	--	NA	--	NA	--	NA	--	2
pH (soil and waste)	TestAmerica	SOP WT05-03.0 (USEPA Method 9045D)	2[A]	NA	--	NA	--	NA	--	NA	--	NA	--	NA	--	2
Paint Filter Test	TestAmerica	SOP WT06-03.0 (USEPA Method 9095B)	1[A]	NA	--	NA	--	NA	--	NA	--	NA	--	NA	--	1

Notes:

1. See Worksheet #23 for Standard Operating Procedure title, revision number, date details.

A. Number of samples is estimated. Number of samples collected will be based on Site evaluation results, field observations and final excavation sizes, etc.

1/day One per day or one per 20 samples, whichever is more frequent. Rinseate blanks not required when dedicated sampling equipment is used.

Freq Frequency.

NA Not Applicable.

No. Number.

SOP Standard Operating Procedure.

TBD To be determined.

QAPP Worksheet #21 Field Sampling Standard Operating Procedure References

Reference Number	Title, Revision Date and/or Number	Originating Organization	Equipment Type	Modified for Project Work? (Y/N)	Comments
FSP (ARCADIS G&M of Michigan, LLC 2008)	*Field Sampling Plan — Soil Sampling Procedures*	ARCADIS	See Field Sampling Plan for specific equipment needs	N	Describes the procedures for soil sampling and the required equipment
FSP (ARCADIS G&M of Michigan, LLC 2008)	*Field Sampling Plan — Groundwater Sampling Procedures*	ARCADIS	See Field Sampling Plan for specific equipment needs	N	Describes the procedures for groundwater sampling and the required equipment
FSP (ARCADIS G&M of Michigan, LLC 2008)	*Field Sampling Plan — XRF Field Screen Procedures*	ARCADIS	See Field Sampling Plan for specific equipment needs	N	Describes use of the XRF as a screening tool for the detection of lead
FSP (ARCADIS G&M of Michigan, LLC 2008)	*Field Sampling Plan — Field Equipment Cleaning and Decontamination Procedures*	ARCADIS	See Field Sampling Plan for specific equipment needs	N	Describes the procedure for field equipment cleaning and decontamination
FSP (ARCADIS G&M of Michigan, LLC 2008) and QAPP Worksheet #27	*Field Sampling Plan* and QAPP Worksheet #27— *Field Samples Handling, Packing, and Shipping Procedures*	ARCADIS	See Field Sampling Plan for specific equipment needs	N	Describes field sample handling, packaging, and shipping procedures
RAWP (ARCADIS G&M of Michigan, LLC 2009).	*Removal Action Work Plan — Confirmation Sampling Procedures*	ARCADIS	See Field Sampling Plan and Removal Action Work Plan for specific equipment needs	N	Describes the procedures for post removal action soil sampling and the required equipment

Notes:

XRF X-Ray Fluorescence.

QAPP Worksheet #23 Analytical Standard Operating Procedure References

Standard Operating Procedure Reference Number	Title, Revision Date, and/or Number	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work? (Y/N)
T-2	*Metals by ICP-AES,* SOP WT03-08.1 Rev. 2, May 30, 2008	Definitive	Metals (Lead)-Soil	ICP-AES	TestAmerica	N
T-3	*Method 6020A/200.8, Metals by ICPMS,* SOP WT-ME-200.8_6020, Rev. 0, January 28, 2008	Definitive	Metals (Lead)-Groundwater	ICP-MS	TestAmerica	N

QAPP Worksheet #24 Analytical Instrument Calibration

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action	Person Responsible for Corrective Action	Standard Operating Procedure Reference[1]
pH meter	Minimum of two points that bracket the expected pH of the samples	Daily/continuing	+/- 0.05 pH units	Inspect system, correct problem, rerun calibration and affected samples.	Analyst	T-1
ICP-AES	Minimum 1 calibration standard and calibration blank. 1 standard (midpoint).	Daily/continuing.	Initial calibration — correlation coefficient $\geq$.995. Continuing calibration — +/- 10% difference.	Inspect system, correct problem, rerun calibration and affected samples.	Analyst	T-2
ICP-MS	Minimum 1 calibration standard and calibration blank. 1 standard (midpoint).	Daily/continuing.	Initial calibration — correlation coefficient $\geq$.995. Continuing calibration — +/- 10% difference.	Inspect system, correct problem, rerun calibration and affected samples.	Analyst	T-3

Notes:

1. SOP reference numbers correspond to SOPs listed in Worksheet #23.

QAPP Worksheet #25 Analytical Instrument and Equipment Maintenance, Testing, and Inspection

Instrument/ Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	Stand Operating Procedure Reference[1]
pH meter	• Periodic inspection of instrument and electrodes • Cleaning of electrodes as needed	pH	Inspect electrodes for breakage or coating	See T-1	See T-1	Inspect system, correct problem, rerun calibration and affected samples	Analyst	Attachment 3
Oven	• Thermometers checked	Not Applicable	Compare to NIST-certified thermometer	record temperature twice daily, calibrate thermometer yearly	Not Applicable	Not Applicable	Analyst	Attachment 3
Balance	• Professional Service Contract	All	Not Applicable	Three times /year	Not Applicable	Not Applicable	Service Contractor	Attachment 3
ICP	• change capillary and pump tubing • check liquid argon tank • replace and realign plasma torch • clean nebulizer and spray chamber	All metals except mercury	Check connections, replace worn equipment	See T-2 and T-3	See T-2 and T-3	Inspect system, correct problem, rerun calibration and affected samples	Analyst	See T-2 and T-3

Notes:

1. Standard Operating Procedure Reference corresponds to SOPs in Worksheet #23.
NIST National Institute of Standards and Technology.

QAPP Worksheet #28-1 Quality Control Samples — Metals (Soil)

Matrix	Soil	**Analytical Method/ SOP Reference**	T-2	**No. of Sample Locations**	Numerous	
Analytical Group	Metals	**Sampler's Name**	Not Applicable			
Concentration Level	All	**Field Sampling Organization**	ARCADIS			
Sampling Standard Operating Procedure	FSP (ARCADIS G&M of Michigan, LLC 2008)	**Analytical Organization**	TestAmerica			
Quality Control Sample	**Frequency/Number**	**Method/Standard Operating Procedures Quality Control Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**Data Quality Indicator**	**Measurement Performance Criteria**
Field Duplicate	One per 10 field samples of similar matrix	RPD < 100%	Qualify data as needed	ARCADIS personnel	Precision — overall	RPD < 100%
Method Blanks	Numerous	< RL	Qualify data as needed or reanalysis of batch	Laboratory personnel	Accuracy/bias contamination	< RL
Equipment Blanks	One per day or one per 20 field samples, whichever is greater	< RL	Qualify data as needed	ARCADIS personnel	Accuracy/bias contamination	< RL
Calibration Verification Standards	Numerous	%R (90-110%)	Reanalysis of batch	Laboratory personnel	Accuracy/bias contamination	%R (90-110%)
Matrix Spike/Matrix Spike Duplicate	One per 20 field samples	%R (75-125%)	Qualify data as needed	Lab personnel and/or ARCADIS personnel	Accuracy/bias	%R (75-125%)
Laboratory Duplicate	One per 20 field samples of similar matrix	RPD < 20%	Qualify data as needed	Laboratory personnel	Precision — overall	RPD < 20%

QAPP Worksheet #28-1 Quality Control Samples — Metals (Soil)

Matrix	Soil	**Analytical Method/ SOP Reference**	T-2	**No. of Sample Locations**	Numerous	
Analytical Group	Metals	**Sampler's Name**	Not Applicable			
Concentration Level	All	**Field Sampling Organization**	ARCADIS			
Sampling Standard Operating Procedure	FSP (ARCADIS G&M of Michigan, LLC 2008)	**Analytical Organization**	TestAmerica			
Quality Control Sample	**Frequency/Number**	**Method/Standard Operating Procedures Quality Control Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**Data Quality Indicator**	**Measurement Performance Criteria**
Laboratory Control Sample	One per batch	%R (80-120%)	Qualify data as needed or reanalysis of batch	Laboratory personnel	Accuracy/bias	%R (80-120%)
Post-Digestion Spike	One per batch	%R (75-125%)	Qualify data as needed	Laboratory personnel	Accuracy/bias	%R (75-125%)

Notes:
*Laboratory control samples/laboratory control sample duplicates used when matrix spike/matrix spike duplicate not client-supplied.
An analytical batch is defined as no more than 20 analytical samples including field samples, blanks, matrix spike/matrix spike duplicates, and laboratory control samples/laboratory control sample duplicates.

LCS	Laboratory control sample.
No.	Number.
RL	Reporting limit.
RPD	Relative percent difference.
SOP	Standard operating procedure.
%D	Percent difference.
%R	Percent recovery.

QAPP Worksheet #28-2 Quality Control Samples — Metals (Groundwater)

Matrix	Groundwater	**Analytical Method/ SOP Reference**	T-3	**No. of Sample Locations**	Numerous
Analytical Group	Metals	**Sampler's Name**	Not Applicable		
Concentration Level	All	**Field Sampling Organization**	ARCADIS		
Sampling Standard Operating Procedure	FSP (ARCADIS G&M of Michigan, LLC 2008)	**Analytical Organization**	TestAmerica		

Quality Control Sample	Frequency/Number	Method/Standard Operating Procedures Quality Control Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Field Duplicate	One per 10 field samples of similar matrix	RPD < 50%	Qualify data as needed	ARCADIS personnel	Precision — overall	RPD < 50%
Method Blanks	Numerous	< RL	Qualify data as needed or reanalysis of batch	Laboratory personnel	Accuracy/bias contamination	< RL
Equipment Blanks	One per day or one per 20 field samples, whichever is greater	< RL	Qualify data as needed	ARCADIS personnel	Accuracy/bias contamination	< RL
Calibration Verification Standards	Numerous	%R (90-110%)	Reanalysis of batch	Laboratory personnel	Accuracy/bias contamination	%R (90-110%)
Matrix Spike/Matrix Spike Duplicate	One per 20 field samples	%R (75-125%)	Qualify data as needed	Lab personnel and/or ARCADIS personnel	Accuracy/bias	%R (75-125%)
Laboratory Duplicate	One per 20 field samples of similar matrix	RPD < 35%	Qualify data as needed	Laboratory personnel	Precision — overall	RPD < 35%

QAPP Worksheet #28-2 Quality Control Samples — Metals (Groundwater)

Matrix	Groundwater	**Analytical Method/ SOP Reference**	T-3	**No. of Sample Locations**	Numerous	
Analytical Group	Metals	**Sampler's Name**	Not Applicable			
Concentration Level	All	**Field Sampling Organization**	ARCADIS			
Sampling Standard Operating Procedure	FSP (ARCADIS G&M of Michigan, LLC 2008)	**Analytical Organization**	TestAmerica			
Quality Control Sample	**Frequency/Number**	**Method/Standard Operating Procedures Quality Control Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**Data Quality Indicator**	**Measurement Performance Criteria**
Laboratory Control Sample	One per batch	%R (80-120%)	Qualify data as needed or reanalysis of batch	Laboratory personnel	Accuracy/bias	%R (80-120%)
Post-Digestion Spike	One per batch	%R (75-125%)	Qualify data as needed	Laboratory personnel	Accuracy/bias	%R (75-125%)

Notes:

*Laboratory control samples/laboratory control sample duplicates used when matrix spike/matrix spike duplicate not client-supplied.
An analytical batch is defined as no more than 20 analytical samples including field samples, blanks, matrix spike/matrix spike duplicates, and laboratory control samples/laboratory control sample duplicates.

LCS Laboratory control sample.
No. Number.
RL Reporting limit.
RPD Relative percent difference.
SOP Standard operating procedure.
%D Percent difference.
%R Percent recovery.

QAPP Worksheet #36 Validation (Steps IIa and IIb) Summary

Step IIa/IIb	Matrix	Analytical Group	Data Purpose	Concentration Level	Validation Criteria	Data Validator (title and organizational affiliation)
Steps IIa and IIb	Soil and Groundwater	Metals	Contaminant delineation, risk assessment, confirmation of remediation	Low, medium, high	USEPA *Contract Laboratory Program National Functional Guidelines for Inorganic Data Review*, October 2002 and USEPA Region II SOPs that apply to SW-846 methods, laboratory control limits, method criteria, QAPP criteria, and professional judgment	Dennis Capria (Data Quality Assurance Manager, ARCADIS)

During the data review process, laboratory qualified and unqualified data are verified against the supporting documentation. Based on this evaluation, qualifier codes may be added, deleted, or modified by the data reviewer. Worksheet 36-A summarizes the data qualification process that will be used by the data reviewer. Results are qualified with the following codes in accordance with the USEPA National Functional Guidelines:

- Concentration (C) Qualifiers

  U The analyte was analyzed for but not detected. The associated value is the analyte instrument detection limit.

  B The reported value was obtained from a reading less than the reporting limit (RL) but greater than or equal to the instrument detection limit (IDL).

- Quantitation (Q) Qualifiers

  N Spiked sample recovery is not within control limits.

  * Duplicate analysis is not within control limits.

- Validation Qualifiers

  J The analyte was positively identified; however, the associated numerical value is an estimated concentration only.

UJ The analyte was not detected above the reported sample detection limit. However, the reported limit is approximate and may or may not represent the actual limit of detection.

R The sample results are rejected.

The "R" flag means that the associated value is unusable. In other words, due to significant quality control problems, the analysis is invalid and provides no information as to whether the compound is present or not. "R" values should not appear on data tables because they cannot be relied upon, even as a last resort.

QAPP Worksheet #36-A Validation Data Qualification Summary

Quality Control Requirements	Frequency	Quality Control Acceptance Criteria	Evaluation Limit	Data Qualification
Initial Calibration (minimum one standard and a blank)	Daily initial calibration prior to sample analysis	All analytes within 10% of expected value	75% to 89%	Non-detect = UJ, Detect = J
			111% to 125%	Non-detect = No action, Detect = J
Second-source calibration verification	Once per initial daily calibration		<75%	Non-detect = R, Detect = J
			>125%	Non-detect = No action Detect = J
Initial calibration blank (ICB)	Once following initial calibration	Analytes must be <RL	Detected sample results <RL and <BAL	U at the RL
			Detected sample results >RL and	U at detected sample concentration

QAPP Worksheet #36-A Validation Data Qualification Summary				
Quality Control Requirements	**Frequency**	**Quality Control Acceptance Criteria**	**Evaluation Limit**	**Data Qualification**
			<BAL	
Calibration verification	Before sample analysis, after every 10 samples, and at the end of the analysis sequence	All analytes within 10% of expected value	75% to 89%	Non-detect = UJ, Detect = J
			111% to 125%	Non-detect = No action, Detect = J
			<75%	Non-detect = R, Detect = J
			>125%	Non-detect = No action Detect = J
Initial calibration verification	Daily, before sample analysis	All analytes within 10% of expected value	75% to 89%	Non-detect = UJ, Detect = J
			111% to 125%	Non-detect = No action, Detect = J
			<75%	Non-detect = R, Detect = J
			>125%	Non-detect = No action Detect = J
Continuing calibration	Following the CCB and before sample analysis, after every 10 samples, and at	Analytes must be <RL	Detected sample results <RL and	U at the RL

QAPP Worksheet #36-A Validation Data Qualification Summary

Quality Control Requirements	Frequency	Quality Control Acceptance Criteria	Evaluation Limit	Data Qualification
blank (CCB)	the end of the analysis sequence		<BAL	
			Detected sample results >RL and <BAL	U at detected sample concentration
Method blank	One per analytical batch	Analytes must be <RL	Detected sample results <RL and <BAL	U at the RL
			Detected sample results >RL and <BAL	U at detected sample concentration
Internal Standards	Added to each sample	Percent Recovery (70-120)	<70% and >120%	Non-detect = UJ, Detect = J
Laboratory-Control Sample	One per prep batch	Percent Recovery (80-120)	50-79%	Non-detect = UJ, Detect = J
			<50%	Non-detect = R, Detect = J
			> 120%	Non-detect = No action, Detect = J
Matrix Spike/Matrix Spike Duplicate	One per batch per matrix	Percent Recovery (75-125)	30-74%	Non-detect = UJ, Detect = J
			<30%	Non-detect = R,

QAPP Worksheet #36-A Validation Data Qualification Summary				
Quality Control Requirements	**Frequency**	**Quality Control Acceptance Criteria**	**Evaluation Limit**	**Data Qualification**
				Detect = J
			>125%	Non-detect = No action, Detect = J
Duplicate	One per batch per matrix	Relative Percent Difference (35% soils; 20% waters)	>35%/20%	Non-detect = UJ, Detect = J

ATTACHMENTS

STANDARD OPERATING PROCEDURE

TestAmerica
Watertown Division

Title: Metals by Inductively Coupled Plasma-Atomic Emission Spectrometry

SOP No.: WT03-08.1
Revision: 2
Effective: 05/30/08

Computer File Name: C:\My Documents\sop\final\ICP.doc

Inorganics Operations Manager Approval	Date	Quality Assurance Approval	Date
Division Manager Approval	Date		

This method may involve hazardous materials, operations and equipment. This method does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed toe, nonabsorbent shoes are a minimum. For specific hazard(s) see reagents, materials and procedure sections of this SOP.

Method Reference:
EPA Method 200.7, (Supplement I, Revision 4.4, May 1994)
EPA Method SW 6010B Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Update III, Rev. 0, December, 1996

Modifications:

Item	Method	Modification
Linear Dynamic Range	200.7	Linear Dynamic Range is not performed. See Sec. 7.2.4
Preparation & Analysis	200.7 and 6010B	Reduction in volume of analysis, along with use of Hot Block

1.0 SCOPE AND APPLICATION

1.1 Analytes: This method is applicable to the following analytes:

Analyte	Abbr.	CAS #
Aluminum	Al	7429-90-5
Antimony	Sb	7440-36-0
Arsenic	As	7440-38-2
Barium	Ba	7440-39-3
Beryllium	Be	7440-41-7
Boron	B	7440-42-8
Cadmium	Cd	7440-43-9
Calcium	Ca	7440-70-2
Chromium	Cr	7440-47-3
Cobalt	Co	7440-48-4
Copper	Cu	7440-50-8
Iron	Fe	7439-89-6
Lead	Pb	7439-92-1
Lithium	Li	7439-93-2
Magnesium	Mg	7439-95-4
Manganese	Mn	7439-96-5
Molybdenum	Mo	7439-98-7
Nickel	Ni	7440-02-0
Potassium	K	7440-02-0
Selenium	Se	7782-49-2
Silver	Ag	7440-22-4
Sodium	Na	7440-23-5
Strontium	Sr	7440-24-6
Thallium	Tl	7440-28-0
Tin	Sn	7440-31-5
Titanium	Ti	7440-32-6
Vanadium	V	7440-62-2
Zinc	Zn	7440-66-6

1.2 All matrices, excluding filtered groundwater samples but including ground water, aqueous samples, TCLP and EP extracts, industrial and organic wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis. Groundwater samples that have been prefiltered and acidified will not need acid digestion. Samples that are not digested must either use an internal standard or be matrix matched with the standards.

2.0 SUMMARY OF METHOD

2.1 An aliquot of sample is accurately measured for sample processing. After cooling, the sample is made up to volume, is mixed and centrifuged or allowed to settle overnight prior to analysis. For the determination of dissolved analytes in a filtered aqueous sample aliquot, no sample preparation steps are required.

2.2 The analysis described in this method involves multielemental determinations by ICP-AES using sequential or simultaneous instruments. The instruments measure characteristic atomic-line emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element specific emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the line spectra are monitored at specific wavelengths by a photosensitive device. Photocurrents from the photosensitive device are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of the analytes. Background must be measured adjacent to the analyte wavelength during analysis.

3.0 INTERFERENCES/COMMENTS

3.1 Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra.
3.2 Subtracting the background emission determined by measurement(s) adjacent to the analyte wavelength peak can usually compensate for background emission and stray light. Spectral scans of samples or single element solutions in the analyte regions may indicate not only when alternate wavelengths are desirable because of severe spectral interference, but also will show whether the most appropriate estimate of the background emission is provided by an interpolation from measurements on both sides of the wavelength peak or by the measured emission on one side or the other. The location(s) selected for the measurement of background intensity will be determined by the complexity of the spectrum adjacent to the wavelength peak. The location(s)used for routine measurement must be free of off-line spectral interference (interelement or molecular) or adequately corrected to reflect the same change in background intensity as occurs at the wavelength peak.
3.3 Spectral overlaps may be avoided by using an alternate wavelength or can be compensated for by equations that correct for interelement contributions, which involves measuring the interfering elements. Some potential on-line spectral interference observed for the recommended wavelengths are given in Attachment III. When operative and uncorrected, these interferences will produce false-positive determinations and be reported as analyte concentrations. The interferences 1isted are only those that occur between method analytes. Only interferences of a direct overlap nature that were observed with a single instrument having a working resolution of 0.035 nm are listed. Users may apply interelement correction factors determined on their instruments within tested concentration ranges to compensate (off-line or on-line) for the effects of interfering elements.
3.4 When interelement corrections are applied, there is a need to verify their accuracy by analyzing spectral interference check solutions as described in Section 7.13. Interelement corrections will vary for the same emission line among instruments because of differences in resolution, as determined by the grating plus the entrance and exit slit widths, and by the order of dispersion. Interelement corrections will also vary depending upon the choice of background correction points. Selecting a background correction point where an interfering emission line may appear should be avoided when practical. Interelement corrections that constitute a major portion of an emission signal may not yield accurate data. Users should not forget that some samples might contain uncommon elements that could contribute spectral interferences.
3.5 The interference effects must be evaluated for each individual instrument whether configured as a sequential or simultaneous instrument. For each instrument, intensities will vary not only with optical resolution but also with operating conditions (such as power, viewing height and argon flow rate). When using the recommended wavelengths given in Attachment III, the analyst is required to determine and document for each wavelength the effect from the known interferences given in the Attachment, and to utilize a computer routine for their automatic correction on all analyses. To determine the appropriate location for off-line background correction, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for their automatic correction on all determinations. If a wavelength other than the recommended wavelength is used, the user must determine and document both the on-line and off-line spectral interference effect from all method analytes and provide for their automatic correction on all analyses. Tests to determine the spectral interference must be done using analyte concentrations that will adequately describe the interference. Normally, 100 mg/L single element solutions are sufficient, however, for analytes such as

iron that may be found at high concentration a more appropriate test would be to use a concentration near the upper LDR limit.

3.6 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by such means as a high-solids nebulizer, diluting the sample, using a peristaltic pump, or using an appropriate internal standard element. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. A high-solids nebulizer, wetting the argon prior to nebulization, using a tip washer, or diluting the sample can control this problem. Also, it has been reported that better control of the argon flow rates, especially for the nebulizer, improves instrument stability and precision; this is accomplished with the use of mass flow controllers.

3.7 Chemical interferences include molecular-compound formation, ionization effects, and solute-vaporization effects. Normally, these effects are not significant with the ICP-AES technique. If observed, they can be minimized by careful selection of operating conditions (such as incident power and observation height), by buffering of the sample, by matrix matching, and by standard-addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

3.8 Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer, and from the buildup of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples. The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element must be estimated prior to analysis. This may be achieved by aspirating a standard containing elements corresponding to either their LDR or a concentration ten times those usually encountered. The aspiration time should be the same as a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals to within a factor of two of the method detection limit should be noted. Until the required rinse time is established, this method requires a rinse period of at least 60 sec between samples and standards. If memory interference is suspected, the sample must be re-analyzed after a long rinse period. Memory effects are suspected if the %RSD of 3 consecutive analyses for an element is >10%.

3.9 Definitions are as listed in the Quality Manual, Section 11, and Appendix 5, unless otherwise defined herein.

4.0 EQUIPMENT AND SUPPLIES

4.1 Inductively coupled plasma emission spectrometer. Perkin Elmer Optima 3000.

4.2 Computer-controlled emission spectrometer with background- correction capability. The spectrometer must be capable of meeting and complying with the requirements described and referenced in Section 2.2.

4.3 Radio-frequency generator compliant with FCC regulations.

4.4 Argon gas supply - High purity grade (99.99%). When analyses are conducted frequently, liquid argon is more economical and requires less frequent replacement of tanks than compressed argon in conventional cylinders.

4.5 A variable speed peristaltic pump is required to deliver both standard and sample solutions to the nebulizer.

4.6 Mass flow controllers to regulate the argon flow rates, especially the aerosol transport gas, are high recommended. Their use will provide more exacting control of reproducible plasma conditions.

5.0 REAGENTS AND STANDARDS

5.1 Standard Stock Solutions - Stock standards may be purchased or prepared from ultra-high purity (UHP) grade chemicals (99.99 to 99.999% pure). TestAmerica - Watertown Division purchases stock standard solution from a commercial vendor. See Attachment I for a list of common stock solutions typically used at TestAmerica - Watertown Division. See Attachment II for typical working standard preparation for CCV, ICV, IEC and calibration solutions found in the following sections.
5.2 Continuing Calibration Verification (CCV) Solution- The CCV solution is used to periodically verify instrument performance during analysis. It should be prepared in the same acid mixture as the calibration standards by combining method analytes at appropriate concentrations. The CCV solution should be prepared from the same standard stock solutions used to prepare the calibration standards and stored in an FEP bottle. Agency programs may specify or request that additional instrument performance check solutions be prepared at specified concentrations in order to meet particular program needs.
5.3 Initial Calibration Verification (ICV) - Analysis of an ICV is required for initial and periodic verification of calibration standards or stock standard solutions in order to verify instrument performance. The ICV must be obtained from an outside source different from the standard stock solutions and prepared in the same acid mixture as the calibration standards. The concentration of the analytes in the ICV solution should be > 1 mg/L. The ICV solution should be stored in a FEP bottle and analyzed as needed to meet data quality needs.
5.4 Spectral Interference Check (IEC) Solutions - When interelement corrections are applied, IEC solutions are needed containing concentrations of the interfering elements at levels that will provide an adequate test of the correction factors. IEC solutions containing (a) 300 mg/L Al, Ca, and Mg; (b) 120 mg/L Fe; (c) 1 mg/L Ag, Cd, Ni, Pb, and Zn; (d) 0.5 mg/L Ba, Be, Co, Cr, Cu, Mn, and V should be prepared in the same acid mixture as the calibration standards and stored in FEP bottles. The concentrations of elements in these solutions must be less than the LDR. These solutions can be used to periodically verify a partial list of the on-line (and possible off-line) interelement spectral correction factors for the recommended wavelengths given in Attachment III.
5.5 Internal Standard Solutions: Internal standards are pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes that are components of the same sample or solution.
5.6 Mixed Calibration Standard Solutions - For the analysis of total recoverable digested samples prepare mixed calibration standard solutions (see Attachment II) by combining appropriate volumes of the stock solutions in 100mL volumetric flasks containing 6 mL conc. HNO_3 and 10 mL conc. HCl and dilute to volume with reagent water. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. To minimize the opportunity for contamination by the containers, it is recommended to transfer the mixed-standard solutions to acid-cleaned, never-used FEP fluorocarbon (FEP) bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentrations can change on aging. Calibration standards not prepared from primary standards must be initially verified using a certified reference solution.

6.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

6.1 Prior to the collection of an aqueous sample, consideration should be given to the type of data required, (i.e., dissolved or total), so that appropriate preservation and pretreatment steps can be taken. The pH of all aqueous samples must be tested immediately prior to aliquoting for processing or "direct analysis" to ensure the sample has been properly preserved. If properly acid preserved, the sample can be held up to 6 months before analysis.
6.2 For the determination of the dissolved elements, the sample must be filtered through a 0.45-micron pore diameter membrane filter at the time of collection or as soon thereafter as practically possible. Acidify the filtrate with (1+1) nitric acid immediately following filtration to pH <2.

6.3 For the determination of total elements in aqueous samples, samples are not filtered, but acidified with (1+1) nitric acid to pH <2 (normally, 3 mL of (1+1) acid per liter of sample is sufficient for most ambient water samples). Following acidification, the sample should be mixed, held for sixteen hours, and then verified to be pH <2 just prior withdrawing an aliquot for processing or "direct analysis". If for some reason such as high alkalinity the sample pH is verified to be >2, more acid must be added and the sample held for sixteen hours until verified to be pH <2.
6.4 Solid samples require no preservation prior to analysis. There is no established holding time limitation for solid samples.

Matrix	Sample Container	Preservation	Prep/Analysis Holding Time	Amount Required
Non-potable water	500 mL plastic	HNO_3 to pH<2	180 days	50 mL
Solids	4 oz plastic or glass	None	180 days	5.0 g

7.0 QUALITY CONTROL

7.1 Sample QC

7.1.1 Preparation Blank: The preparation blank is an aliquot of reagent or a combination of reagents that are prepared in the same manner as the preparation procedures for the field samples. One preparation blank is prepared with each batch of field samples. See the TestAmerica - Watertown Division Sample Preparation for Metals Analysis by FLAA/ICP (WT03-07) for the preparation procedure. Analyze the sample as specified in Section 8.3. If the blank contains a result greater than the reporting limit for that metal then the entire preparation batch should be re-prepared and re-analyzed for that metal. Alternatively, the sample results for that metal must be flagged appropriately.

7.1.2 Laboratory Control Sample: The LCS consists of an aliquot of reagent. The LCS is spiked with the same analytes at the same concentrations as the matrix spike and carried through the same entire preparation scheme as the samples, including sample digestion. See the TestAmerica - Watertown Division Sample Preparation for Metals Analysis by FLAA/ICP (WT03-07) for the preparation procedure. When the results of the matrix spike analysis indicates a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

7.1.2.1 Calculate the percent recovery of the spiked analytes. The percent recoveries of the spiked analytes should be within laboratory established control limits.

7.1.2.2 If the percent recovery of a target analyte falls outside the control limit, the LCS should be re-analyzed once. If the percent recovery of the same target is out of control, then the sample results for the affected analyte must be flagged for the out of control LCS or the sample batch must be re-prepared and re-analyzed.

7.1.3 Matrix Spike: Sample homogeneity and the chemical nature of the sample matrix can affect analyte recovery and the quality of the data. Taking separate aliquots from the sample for replicate and fortified analyses can in some cases assess the effect. See the TestAmerica - Watertown Division Sample Preparation for Metals Analysis by FLAA/ICP (WT03-07) for the preparation procedure.

7.1.3.1 The laboratory must add a known amount of each analyte to a minimum of 10% of the routine samples. In each case the MS or MSD aliquot must be a duplicate of the aliquot used for sample analysis and the spike added prior to sample preparation. For water samples, the added analyte concentration must be the same as that used in the

LCS. For solid samples, however, the concentration added should be expressed as mg/kg. Over time, samples from all routine sample sources should be fortified.

7.1.3.2 Calculate the percent recovery of the spiked analytes. Recovery calculations are not required if the concentration added is less than 30% of the sample background concentration. The percent recoveries of the spiked analytes should be within laboratory established control limits.

7.1.3.3 Calculate the relative percent difference (RPD) between the MS and the MSD result for each target analyte.

7.1.3.4 If the recovery or RPD of any analyte falls outside the acceptance recovery range, the recovery problem encountered with the fortified sample is judged to be matrix related, not system related. The sample results for that analyte should then be flagged appropriately.

7.1.4 Duplicates: To help determine the precision of the instrument, two separate aliquots of the same prepared sample must be analyzed. The relative percent difference (RPD) between the two measurements for each target metal must meet the RPD limit of MS/MSDs. If the RPD exceeds this limit, the duplicate samples are re-analyzed. If the RPD exceeds the limit a second time, the data for the affected analyte is flagged appropriately.

7.1.5 Analytical Spike: To determine the accuracy of the analyses, at least one sample in each analytical batch is spiked with the target analytes <u>after</u> the preparation procedure. This analysis is referred to as the post-digestion or analytical spike. The solution spiked into the samples is the ICV solution (see Attachment II for ICV standard preparation information). Calculate the percent recovery for each spiked target analyte. The recovery must be 85-115% for each target analyte. If the recovery for any target falls out of this range, the sample should be re-analyzed. If the recovery still fails the acceptance criteria, the sample results should be flagged to indicate matrix interference.

7.1.6 Internal Standards: The internal standard solution (see Attachment II for Internal standard solution preparation information) is continuously mixed with all samples analyzed on the instrument. A percent recovery is calculated by the instrument software and is used to determine whether or not there is potential matrix interference. *At this time, there are no acceptance criteria for the percent criteria for the recovery of the internal standards.* The analyst determines the acceptability of the percent recoveries. If the recoveries are low, the sample must be diluted and re-analyzed. If the recoveries are still low following dilution and re-analysis, the data must be flagged appropriately to indicate matrix interference.

7.2 Instrument QC

7.2.1 Initial Calibration Verification (ICV): When beginning the use of this method, on a quarterly basis, after the preparation of stock or calibration standard solutions or as required to meet data- quality needs, verify the calibration standards and acceptable instrument performance with the preparation and analyses of a ICV (see Attachment II for ICV preparation information). To verify the calibration standards the determined mean concentrations from 3 analyses of the ICV must be within 10% (5% for 200.7) of the stated values. If the calibration standard cannot be verified, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before either proceeding on with analyses.

7.2.2 Continuing Calibration Verification (CCV): solution - For all determinations the laboratory must analyze the CCV solution (see Attachment II for CCV solution preparation information) immediately following daily calibration, after every tenth sample (or more frequently, if required) and at the end of the sample run. Analysis of the CCV solution immediately following calibration must verify that the instrument is within 10% of calibration (within 5% for EPA 200.7)with a relative standard deviation <3% from replicate integrations. Subsequent analyses of the CCV solution must be within 10% of calibration.

7.2.2.1 If the calibration cannot be verified within the specified limits, reanalyze the CCV solution.

7.2.2.2 If the second analysis of the CCV solution confirms calibration to be outside the limits, sample analysis must be discontinued, the cause determined, corrected and/or the instrument recalibrated.

7.2.2.3 All samples following the last acceptable CCV solution must be reanalyzed. The analysis data of the CCV solution must be kept on file with the sample analyses data.

7.2.3 Reagent Blank: A reagent blank is analyzed immediately following daily calibration, after every tenth sample and at the end of the sample run. Analysis of the reagent blank should meet the same acceptance criteria as a Preparation Blank (see Sec. 7.1.7).

7.2.3.1 If a target analyte result fails the acceptance criteria, reanalyze the reagent blank.

7.2.3.2 If the same target analyte result fails the acceptance criteria in the second analysis of the reagent blank, sample analysis must be discontinued, the cause determined, corrected and/or the instrument recalibrated.

7.2.3.3 All samples following the last acceptable CCV solution must be reanalyzed. The analysis data of the reagent blanks must be kept on file with the sample analyses data.

7.2.4 Linear Dynamic Range (LDR) - The upper limit of the LDR must be established for each wavelength utilized. It must be determined from a linear calibration prepared in the normal manner using the established analytical operating procedure for the instrument. When an appropriate level standard recovers within 10% of true value, the laboratory can report any data up to 90% of that level. With this option chosen, there is no need to re-validate LDRs on an annual basis, as the complete linear range is not being used. This information is documented and kept on file.

7.2.5 Spectral Interference Check (IEC) Solutions

7.2.5.1 When interelement corrections are applied, IEC solutions are needed containing concentrations of the interfering elements at levels that will provide an adequate test of the correction factors. See Attachment II for the IEC solution preparation information.

7.2.5.2 If the apparent concentration was false positive, the new factor is added to the IEC factor in the computer method. If the apparent concentration was a negative result, the new factor is subtracted from the IEC factor in the computer method. The new correction factors are then entered into and saved with the computer's analytical method. The raw data of the entire analytical sequence following the IEC factor update is processed using the new IEC factors.

7.2.6 Method Detection Limit Study - The Method Detection Limit (MDL) is the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. The MDL does not imply that the concentration of a substance can be quantified, only that it can be accurately identified. MDL studies are the analysis of at least seven replicates of laboratory grade water spiked at a low level. The MDL is calculated as the standard deviation of these results multiplied by the appropriate Student's t value. For additional details, see Section 11.3 of the TestAmerica Watertown Quality Manual.

Summary of QC Frequency

	Preparation Blank	Matrix Spike/Matrix Spike Duplicate	Lab Duplicate	Lab Control Standard	Analytical Spike	Internal Standards
Frequency	1 per batch of 20	1 per batch of 20	1 per batch of 20	1 per batch of 20	As needed	Each analysis
Acceptance Limits	Less than the highest of (1) MDL; (2) 5% of reg. Limit: (3) 5% of highest sample	Programmed into LIMS based on historical data	Programmed into LIMS based on historical data	85-115% Recovery for 200.7; 80-120% Recovery for SW-6010 B	85-115% Recovery	Not established by this SOP at this time
Corrective Action	Re-prepare the prep batch	If the LCS is acceptable, flag the data to indicate matrix interference; if LCS not acceptable, re-prepare the prep batch.	Re-analyze the duplicate samples; if the criteria fails a second time, flag the affected analytes appropriately	Re-prepare the prep batch	Flag the data to indicate matrix interference	Dilute sample and re-analyze; if still low, flag data for matrix interference.

Calibration Acceptance Summary

Step	Standards	Type	Control Limit		Frequency
Method # 200.7 and 6010 B			*EPA 200.7*	*SW-6010 B*	
Initial Cal	Calibration blank and 1 standard	Linear			Daily
ICV	1 Standard	Single Point	95-105	90-110	Once, Immediately following curve
CCV	See Attachment II for concentrations	Single Point	95-105	90-110	Immediately following curve and once every 10 samples

8.0 PROCEDURE

8.1 Sample Preparation

8.1.1 Dissolved Metals: If the sample has not been filtered through a 0.45µm filter prior to reaching the laboratory then the sample must be filtered. Assuming the sample meets the pH criteria, the sample is analyzed as is.

8.1.2 Total Metals: For aqueous sample requiring preparation, see the Sample Preparation for Metals Analysis by FLAA and ICP-AES SOP (WT03-07).

8.2 Calibration – Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in Attachment II. Typically, the concentration of the analytes in the standard is 10ppm. Flush the system with the calibration blank between each standard or as the manufacturer recommends. (Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.) The calibration curve must consist of a minimum of a blank and a standard.

8.3 Sample Analysis

8.3.1 Set up the instrument with proper operating parameters established as detailed below. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 minutes of operation prior to calibration). See Attachment IV for a list of typical plasma operating conditions.

8.3.2 Specific wavelengths are listed in Attachment III. Other wavelengths may be substituted if they can provide the needed sensitivity and are corrected for spectral interference. Because of differences among various makes and models of spectrometers, specific instrument operating conditions cannot be provided. The instrument and operating conditions utilized for determination must be capable of providing data of acceptable quality to the program and data user. The analyst should follow the instructions provided by the instrument manufacturer unless other conditions provide similar or better performance for a task. Operating conditions for aqueous solutions usually vary from 1100 to 1200 watts forward power, 14 to 18 mm viewing height, 15 to 19 liters/mm argon coolant flow, 0.6 to 1.5 L/min argon nebulizer flow, 1 to 1.8 mL/min sample pumping rate with a 1 minute pre-flush time and measurement time near 10 seconds per sample for simultaneous instruments.

8.3.3 The plasma operating conditions need to be optimized prior to use of the instrument. This routine is not required on a daily basis, but only when first setting up a new instrument or following a change in operating conditions. The following procedure is recommended or follows manufacturer's recommendations. The purpose of plasma optimization is to provide a maximum signal to background ratio for some of the least sensitive elements in the analytical array. The use of a mass flow controller to regulate the nebulizer gas flow or source optimization software greatly facilitates the procedure.

8.3.3.1 Ignite the radial plasma and select an appropriate incident RF power. Allow the instrument to become thermally stable before beginning, about 30 to 60 minutes of operation. While aspirating a 1000 ug/L solution of yttrium, follow the instrument manufacturer's instructions and adjust the aerosol carrier gas flow rate through the nebulizer so a definitive blue emission region of the plasma extends approximately from 5 to 20 mm above the top of the load coil Record the nebulizer gas flow rate or pressure setting for future reference. The yttrium solution can also be used for coarse optical alignment of the torch by observing the overlay of the blue light over the entrance slit to the optical system.

8.3.3.2 After establishing the nebulizer gas flow rate, determine the solution uptake rate of the nebulizer in mL/min by aspirating a known volume of calibration blank for a period of at least three minutes. Divide the volume aspirated by the time in minutes and record the uptake rate; set the peristaltic pump to deliver the rate in a steady even flow.

8.3.3.3 Profile the instrument to align it optically as it will be used during analysis. The following procedure can be used for both horizontal and vertical optimization in the radial mode, but is written for vertical. Aspirate a solution containing 10 ug/L of several selected elements. These elements can be As, Se, Tl or Pb as the least sensitive of the elements and most needing to be optimize or others representing analytical judgement (V, Cr, Cu, Li and Mn are also used with success). Collect intensity data at the wavelength peak for each analyte at 1 mm intervals from 14 to 18 mm above the load coil. (This region of the plasma is referred to as the analytical zone.) Repeat the process using the calibration blank. Determine the net signal to blank intensity ratio for each analyte for each viewing height setting. Choose the height for viewing the plasma that provides the best net intensity ratios for the elements analyzed or the highest intensity ratio for the least sensitive element. For optimization in the axial mode, follow the instrument manufacturer's instructions.

8.3.3.3.1 The instrument operating condition finally selected as being optimum should provide the lowest reliable instrument detection limits and method detection limits.

8.3.3.3.2 If either the instrument operating conditions such as incident power or nebulizer gas flow rate are changed, or a new torch injector tube with a different orifice internal diameter is installed, the plasma and viewing height should be re-optimized.

8.3.3.3.3 After completing the initial optimization of operating conditions, but before analyzing samples, the laboratory must establish and initially verify an interelement spectral interference correction routine to be used during sample analysis. A general description concerning spectral interference and the analytical requirements for background correction in particular is discussed in the section on interferences (Section 7.2.5). Criteria for determining an interelement spectral interference is an apparent positive or negative concentration for the analyte that falls within $\pm$ one reporting limit from zero. The upper control limit is the analyte instrument detection limit. Once established the entire routine must be periodically verified every six months. Only a portion of the correction routine must be verified more frequently or on a daily basis. Initial and periodic verification of the routine should be kept on file. Special cases where continual verification is required are described elsewhere.

8.3.3.3.4 Before daily calibration and after the instrument warm-up period, the nebulizer gas flow rate must be reset to the determined optimized flow. If a mass flow controller is being used, it should be set to the recorded optimized flow rate, In order to maintain valid spectral interelement correction routines the nebulizer gas flow rate should be the same (<2% change) from day to day.

8.3.3.4 Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on each particular instrument. All measurements must be within the instrument linear range where the correction equations are valid.

8.3.4 For each sample analyzed, aspirate 3 replicates. The %RSD must be <10% for each sample.

9.0 CALCULATIONS/DATA REDUCTION AND INTERPRETATION

The ICP data systems calculate the final concentration of each sample automatically. If dilutions were performed, the appropriate factors must be applied to sample values. All results should be reported to two significant figures. For additional information, see Section 12.0, TestAmerica Watertown Quality Manual.

10.0 METHOD PERFORMANCE

Quality control limits are generated based on historical data achieved at TestAmerica - Watertown. These limits are entered into the LIMS for purposes of judging acceptance. This method was initially validated by TestAmerica - Watertown in January and February, 2003.

11.0 POLLUTION CONTROL

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability).

12.0 WASTE MANAGEMENT

Laboratory waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to SOP WT07-02.0, Waste Disposal.

13.0 REFERENCES/CROSS REFERENCES

13.1 Quality Manual – TestAmerica Watertown
13.2 SOP WT07-02 – Waste Disposal
13.3 SOP CP01-01 – Writing a Standard Operating Procedure (SOP)
13.4 TestAmerica – Watertown Division Sample Preparation for Metals Analysis by FLAA and ICP-AES SOP (WT03-07)

14.0 ATTACHMENTS

14.1 Attachment I: Typical Stock solutions Received from CPI and Spex

Stock target analyte standards are typically received as certified solutions from a manufacturer or supplier. Typical standards received from typical suppliers are:

Spex	Internal Standard			
		10,000 ug/mL Y	Cat#ply2-2x	2% HNO_3
		10,000 ug/mL Ga	Cat#plga2-3x	5% HNO_3
Spex	Calibration I	Custom Multi-element Standard	Cat.#xnetia-1	5% HNO_3
Spex	Calibration II	Quality Control Standard 21	Cat.#qc-21-500	5% HNO_3
		1,000ug/ml Sn	Cat.#plfn5-2y	20% HCL
Spex	Calibration III	1,000ug/ml Ag	Cat.#plag2-2y	2% HNO_3
CPI	ICV I		P/NS4400-0005	5% HNO_3
			P/N4400-130002	15% HCl
CPI	ICV II		P/N4400-130053	5% HNO_3
CPI	ICV III	1,000ug/mL Ag	P/N4400-1000511	2% HNO_3
Spex	CCV I	Custom Multi-element Standard	Cat#xnetia-1	5% HNO_3
Spex	CCV II	Quality Control Standard 21	Cat#qc-21-500	5% HNO_3
		1,000 ug/mL Ag	P/N4400-1000511	2% HNO_3

14.2 Attachment II: Typical Preparations for Working Standard Solutions

Standard		Final Volume	Matrix
Internal standard:	10mL Y + 10mL Ga	200mL	6% HNO3/ 10% HCl
Calibration Standard 1	10mL Custom Multi-element	100mL	6% HNO3/ 10% HCl
Calibration Standard 2	10 mL Quality Control Standard + 1 mL Sn	100mL	6% HNO3/ 10% HCl
Calibration Standard 3	0.2 mL Ag Standard	100mL	6% HNO3/ 10% HCl
ICV 1	5 mL stock standard P/NS4400-0005 + 5 mL stock standard P/N4400-130002	100mL	6% HNO3/ 10% HCl
ICV II	10 mL stock standard P/N4400-130053	100mL	6% HNO3/ 10% HCl
ICV III	0.1 mL stock standard P/N4400-1000511	100mL	6% HNO3/ 10% HCl
IEC A	6mL interferant A	100mL	6% HNO3/ 10% HCl
IEC AB	6mL interferant A + 1 mL Analytes B	100mL	6% HNO3/ 10% HCl
CCV I	5mL Custom Multi-element Standard	100mL	8%HNO3/ 4%HCL
CCV II	5mL Quality Control Standard 21 + 0.5mL Sn + 0.1mL Ag Standard	100mL	8%HNO3/ 4%HCL

14.3 Attachment III: Wavelengths and Potential Interferants

Analyte	(nm)	Interferant
Ag	328.068	Ce,Ti,Mn
Al	308.213	V,Mo,Ce,Mn
As	193.695	V,Al,Co,Fe,Ni
B	249.772	None
Ba	233.528	None
Be	234.861	V,Ce
Ca	315.885	Co,Mo,Ce
Cd	214.438	Ni,Ti,Fe,Ce
Co	228.614	Ti,Ba,Cd,Ni,Cr,Mo,Ce
Cr	267.706	Be,Mo,Ni
Cu	324.753	Mo,Ti
Fe	238.864	None
Ga	294.363	None
K	766.491	None
Li	670.784	None
Mg	279.079	Ce
Mn	257.608	Ce
Mo	202.030	Ce
Na	589.602	None
Ni	231.604	Co,Tl
Pb	220.351	Co,Al,Ce,Cu,Ni,Ti,Fe
Sb	206.836	Cr,Mo,Sn,Ti,Ce,Fe
Se	196.025	Fe
Sn	189.927	Mo,Ti,Fe,Mn,Si
Sr	460.734	None
Ti	368.519	None
Tl	190.794	Ti,Mo,Co,Ce,Al,V,Mn
V	292.396	Mo,Ti,Cr,Fe,Ce
Y	371.032	None
Zn	213.856	Ni,Cu,Fe

14.4 Attachment IV: ICP Plasma Operating Parameters

Source Equilibration Delay: 15 seconds
Elements: ALL
Plasma (L/min): 15
Auxilary (L/min): 0.3
Nebulizer (L/min): 0.95
Power (Watts): 1425
View Height (mm): 14
Plasma View: Radial

14.5 The following are the flags that could routinely be expected to be used for this analysis. The usages that are listed are not meant to be all-inclusive, they are only to serve as examples.

FLAG	DESCRIPTION	USAGE
*	See Case Narrative	Information not covered by any flag that must be relayed on the final report; provide details to Operations Manager for reporting
B	Blank is contaminated	Analyte of concern is found in the blank at a level higher than is acceptable in the method
C	Standard outside of control limits	Percent recovery of a CCV or LCS is outside of control limits
D	Diluted for analysis	Sample diluted for analysis
E	TCLP temp exceeds limits	TCLP extraction performed outside of method range of 21 - 25C
F	Sample filtered in lab	Sample was received without field filtering, as is required by method or regulation
J	Estimated Concentration	Sample concentration is over calibration or in doubt for some reason (i.e., potential loss in transfer, leakage, ...)
M	Matrix Interference	Sample quantitation is difficult due to matrix interference (i.e., peak shape is not normal, recovery of matrix spike is out of control, ...)
P	Improperly preserved sample	Sample is not correctly preserved, whether chemically or by temperature
Q	Results confirmed via re-analysis	Sample result is confirmed via re-analysis due to unexpected initial result; both analyses are in agreement with each other
S	Sediment present	Sample contains sediment which should not be present in a filtered sample

15.0 CONTINGENCIES

Any deviations from this SOP must be brought to the attention of the appropriate Operations Manager, the Laboratory Manager, or the QA Coordinator. This deviation must be documented on a Corrective Action Report and submitted to the QA Coordinator.

Title: Method 6020A / 200.8
Metals by ICPMS

Approvals (Signature/Date):

Michael Miller Operations Manager	Date	Traci Saeger Health & Safety Manager / Coordinator	Date
Paul Junio Quality Assurance Manager	Date	Karri Warnock Laboratory Director	Date

Facility Distribution No. ___________ **Distributed To:**________________________

1.0 SCOPE AND APPLICATION

1.1. This procedure describes multi-elemental analysis by inductively coupled plasma-mass spectrometry (ICP-MS) based on SW-846 protocol as described in EPA Method 6020A and 200.8. The source method lists twenty-three elements approved for analysis by ICP/MS (Al, Sb, As, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Ni, K, Se, Ag, Na, Tl, V and Zn). Additional elements may be included provided that the method performance criteria presented in Section 9 is met.

Analyte	MDL	LOQ	Units	MRL	Units
Aluminum	150	500	ug/L	12000	ug/kg
Antimony	0.12	0.40	ug/L	10	ug/kg
Arsenic	0.12	0.40	ug/L	10	ug/kg
Barium	0.12	0.40	ug/L	10	ug/kg
Beryllium	0.12	0.40	ug/L	10	ug/kg
Boron	6.0	20	ug/L	500	ug/kg
Cadmium	0.12	0.40	ug/L	10	ug/kg
Calcium	150	500	ug/L	12000	ug/kg
Chromium	0.12	0.40	ug/L	10	ug/kg
Cobalt	0.12	0.40	ug/L	10	ug/kg
Copper	6.0	20	ug/L	500	ug/kg
Iron	150	500	ug/L	12000	ug/kg
Lead	0.12	0.40	ug/L	10	ug/kg
Magnesium	150	500	ug/L	12000	ug/kg
Manganese	0.12	0.40	ug/L	10	ug/kg
Molybdenum	0.12	0.40	ug/L	10	ug/kg
Nickel	6.0	20	ug/L	500	ug/kg
Potassium	150	500	ug/L	12000	ug/kg
Selenium	0.12	0.40	ug/L	10	ug/kg
Silver	0.12	0.40	ug/L	10	ug/kg
Sodium	150	500	ug/L	12000	ug/kg
Strontium	6.0	20	ug/L	500	ug/kg
Thallium	0.12	0.40	ug/L	10	ug/kg
Tin	6.0	20	ug/L	500	ug/kg
Titanium	6.0	20	ug/L	500	ug/kg
Vanadium	0.12	0.40	ug/L	10	ug/kg
Zinc	6.0	20	ug/L	500	ug/kg

1.2. This procedure also describes the requirements for performing analysis of ground waters, surface waters and drinking water.

1.3. The procedure is applicable to the analysis of waters, soils, and wastes. No digestion is required prior to analysis for dissolved elements in water samples, but the samples must be filtered and preserved prior to analysis. Preliminary acid digestion is required for groundwater, aqueous samples, sludges, sediments, and other solid wastes for which total (acid- leachable) elements are requested.

1.4. This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

1.5 On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in Section in the Quality Assurance Manual.

2.0 SUMMARY OF METHOD

Aqueous sample, digestates, leachates, etc. are nebulized into a spray chamber where a stream of argon carries the sample aerosol through a quartz torch and injects it into a R.F. plasma. There the sample is decomposed and desolvated. The ions produced are entrained in the plasma gas and by means of a water-cooled, differentially pumped interface, introduced into a high-vacuum chamber that house a quadrupole mass spectrometer. The ions are sorted according to their mass-to-charge ratio and measured with a detector.

3.0 DEFINITIONS

3.1 See Appendix 6, TestAmerica Watertown Quality Assurance Manual.
3.2 *Dissolved Metals* - Those elements which pass through a 0.45 um membrane filter (sample is acidified after filtration).
3.3 *Suspended Metals* - Those elements which are retained by a 0.45 um membrane filter.
3.4 *Total Metals* - The concentration determined on an unfiltered sample following vigorous acid digestion.
3.5 *Tuning Solution* - This is a multi-element solution containing analytes which are representative of the entire mass range capable of being scanned by the instrument. It is used to optimize the sensitivity of the instrument and to verify the mass resolution meets method criteria.

4.0 INTERFERENCES

Isobaric Interferences occur when an isotope of one element is at the same nominal mass as an isotope of another element (e.g. Mo^{98} and Ru^{98}). Corrections for isobaric interferences may be made by measuring the intensity due to the interfering element at another isotope and using its natural abundance ratios to correct for its presence at the analytical mass of interest. Most commonly used corrections for isobaric interferences are already present as default interference equations in the ELAN NT software.
4.1. Care should be taken that the isotope measured for correction purposes does not suffer from overlap with other isotopes that may be present in the sample.
4.2 Molecular interferences are caused by molecular species formed in the plasma with plasma or matrix ions (examples of common molecular interferences include ArCl, ClO, Nitrogen dimer, oxygen dimer, oxide species, double charged species, etc.) Predictions about the type of molecular interferences may be made using knowledge about the sample matrix. Molecular interferences can often be corrected for in the same manner as isobaric interferences, i.e., measuring the intensity present at another isotope and using isotope ratios to calculate the amount of the interfering species. For example, corrections for interferences of $Ar^{40}Cl^{35}$ on As at mass 75 may be made by measuring the intensity of ArCl present at mass 77 ($Ar^{40}Cl^{37}$) and converting to the apparent intensity of ArCl at mass 75 by using the isotopic ratio of Cl^{37} to Cl^{35}. Method 200.8 requires the use of several such corrections which are present in the ELAN NT 200.8 Method.

5.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), Radiation Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.
5.1 Safety glasses should be worn at all times when handling samples, reagents, or when in the vicinity of others handling these items.

5.2 Liquid argon represents a potential cryogenic hazard and safe handling procedures should be used at all times when handling liquid argon tanks.
5.3 The ICP plasma emits strong UV light and is harmful to vision. All analysts must avoid looking directly at the plasma. The ELAN 6000 is fully interlocked to protect the user from dangers such as high voltages, radio frequency generators, and intense ultra-violet light. At no time should the operator attempt to disable these interlocks or operate the ELAN 6000 if any safety interlock is known to be disabled or malfunctioning.
5.4 Spilled samples, reagents, and water should be cleaned up from instrument and autosampler surfaces immediately. In the case of acid spills the acid should be neutralized with sodium bicarbonate solution before cleanup.
5.5 All additional company safety practices should be followed at all times.
5.6 PRIMARY MATERIALS USED - The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material[1]	Hazards	Exposure Limit[2]	Signs and symptoms of exposure
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.

1 – Always add acid to water to prevent violent reactions.
2 – Exposure limit refers to the OSHA regulatory exposure limit.

6.0 EQUIPMENT AND SUPPLIES

6.1 Perkin-Elmer ELAN® 6000 ICP-MS system. This includes ELAN 6000 instrument, computer system, ELAN NT software, printer, and autosampler.
6.2 Peristaltic pump tubing:
- 6.2.1 Black/Black - 0.75 mm i.d. (for sample introduction).
- 6.2.2 Yellow/Orange - 0.51 mm i.d. (for internal standard introduction).
- 6.2.3 Purple/White - 2.79 mm i.d. (for drain).
- 6.2.4 Red/Red - 1.14 mm i.d. (for rinse station).
- 6.2.5 Blue/Blue - 1.65 mm i.d. (for making connections).
- 6.2.6 Purple/Purple -2.06 mm i.d. (for making connections).

6.3 T-connector, polypropylene, 1/16 inch i.d. (PE Part # B019-8201; Cole Parmer Part Number: H-06365-77) for hooking up on-line addition of internal standards.
6.4 Calibrated mechanical pipettes.
- 6.4.1 10-100 uL.
- 6.4.2 100 - 1000 uL.

6.4.3 1000 - 5000 uL.
6.5 Metal-free plastic pipette tips.
6.6 15-mL plastic Autosampler tubes with caps (PE Part # B019-3233).
6.7 50-mL plastic Autosampler tubes with caps (PE Part # B019-3234).
6.8 Argon gas: High purity grade (99.99%).

7.0 REAGENTS AND STANDARDS

All reagents may contain impurities that may affect the integrity of the analytical results. Due to the high sensitivity of ICP-MS, high-purity reagents, water, and acids must be used whenever possible. All acids used for this method must be of ultra high-purity grade. Nitric acid is preferred for ICP-MS in order to minimize polyatomic interferences. It should be noted that hydrochloric acid is required to maintain stability in solutions containing antimony and silver. When hydrochloric acid is used, corrections for poly-atomic ion interferences must be used.

7.1 Nitric acid, concentrated. Ultra-pure from sub-boiling distillation is preferred. Suggested suppliers include: Seastar ™- Sub-boiling distilled grade, Sidney, BC; J. T. Baker - ULTREX® Grade; and Fisher - Optima Grade.
7.2 Hydrochloric acid, concentrated. Ultra-pure from sub-boiling distillation is preferred. Suggested suppliers include: Seastar™ - Sub-boiling distilled grade, Sidney, BC; J. T. Baker - ULTREX® Grade; and Fisher - Optima Grade.
7.3 Reagent water equivalent to ASTM Type I water (ASTM D 1193).
7.4 1:1 (vol/vol) nitric acid – Prepare by adding 50 mL concentrated nitric acid to 50 mL reagent water in a clean 125 mL HDPE bottle.
7.5 Single element stock solutions of the following elements:
7.5.1 Beryllium - PE Part # N930-0172.
7.5.2 Magnesium - PE Part # N930-0179.
7.5.3 Cobalt - PE Part # N930-0113.
7.5.4 Rhodium - PE Part # N930-0144.
7.5.5 Indium - PE Part # N930-0124.
7.5.6 Barium - PE Part # N930-0181.
7.5.7 Cerium - PE Part # N930-0110.
7.5.8 Lead - PE Part # N930-0175.
7.6 Tuning solution Stock: 10 mg/L Be, Mg, Co, Rh, In, Ba, Ce, and Pb. Prepare by pipetting 500 μL of each 1000 mg/L single element stock solutions into a 50-mL autosampler tube. Add 1 mL 1:1 nitric acid and dilute to 50 mL with reagent water.

***Note**: Instructions are provided for making all reagents and standards from raw materials. It is recommended that reagents and standards are purchased pre-made by the vendor.*
***Note**: The suggested solution in Method 6020 does not meet the tuning requirements of the manufacturer for the ELAN 6000. The tuning solution defined in this section of the SOP allows all manufacturer tuning parameters to be met while also meeting the stated requirements of the tuning solution in Section 5.8 of Method 6020, Revision 0.*

7.7 Tuning solution: 10 μg/L Be, Mg, Co, Rh, In, Ba, Ce, and Pb. Prepare by pipetting 1 mL of Tuning Stock solution into a 1-Liter flask filled with 200 mL of reagent water, add 10 mL of concentrated nitric acid and dilute to 1 Liter with reagent water and mix well.
7.8 Internal Standard Stock Solution: 10 mg/L Li^6, Sc, Y, In, Rh, Tb, Ho, and Bi; 50 ppm Ge. Prepare by pipetting 500 μL of each of the following 1000 mg/L stock solutions into a 50-mL autosampler tube:
7.8.1 Rhodium - PE Part # N930-0144.
7.8.2 Holmium - PE Part # N930-0123.

7.8.3 Add 5 mL of a stock solution containing 100 mg/L of the following: Li^6, Sc, Y, In, Tb, and Bi (available from VHG Labs, Cat No. LIS-100).
7.8.4 Add 2.5 mL of 1000 mL germanium stock solution - PE Part # N930-0120.
7.8.5 Add 1 mL 1:1 nitric acid and dilute to 50 mL with reagent water.

Note: *All solutions including calibration blanks, calibration standards, samples, quality control standards, and quality control samples must be spiked with the same level of the internal standard stock solution. For the work described in this SOP 100 L of the stock solution was spiked in per 50 mL of solution.*

7.9 Standard stock solutions. The following combinations are suggested.
7.9.1 Calibration Stock 1 - containing 20 ppm of Al, As, Sb, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Tl, Th, U, V, Zn.
7.9.2 Calibration Stock 2 - containing 20 ppm of Ag and Ba.
7.9.3 Calibration Stock 3 - containing 100 ppm of Na, Ca, Mg, K, and Fe

7.10 ICV (Independent Calibration Verification) stock - the ICV stock MUST BE from a source independent of that used for calibration. The concentrations of the analytes in the ICV are prepared near the mid-point of the calibration range.
7.10.1 ICV Stock 1 - containing 10 ppm of Al, As, Sb, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Tl, Th, U, V, Zn.
7.10.2 ICV Stock 2 - containing 10 ppm of Ag and Ba
7.10.3 ICV Stock 3 - containing 100 ppm of Na, Ca, Mg, K, and Fe

7.11 Calibration standards: Prepare fresh single or multi-element calibration standards daily as is appropriate for the analysis. The following calibration standard combinations are recommended and have been found to work for a wide variety of samples:
7.11.1 Calibration Blank: A solution containing 1% (v/v) nitric acid in reagent water. Fill a 50-mL autosampler tube with approximately 20 mL of reagent water. Pipette 1 mL of 1:1 (vol/vol) nitric acid into a 50-mL autosampler tube and dilute to 50 mL with reagent water.
7.11.2 Calibration Standard 1: 0.4 μg/L of Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Tl, Th, U, V, and Zn; and 100 μg/L Na, Ca, Mg, K, and Fe. Fill a 50-mL autosampler tube with approximately 20 mL of reagent water. Add 1 mL of 1:1 nitric acid. Pipette 25 μL of Calibration Stock 1, 25 μL of Calibration Stock 2, and 50 μL of Calibration Stock 3 to the tube and dilute to 50 mL with reagent water.
7.11.3 Calibration Standard 2: 20 μg/L of Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Tl, Th, U, V, and Zn; and 1mg/L Na, Ca, Mg, K, and Fe. Fill a 50-mL autosampler tube with approximately 20 mL of reagent water. Add 1 mL of 1:1 nitric acid. Pipette 50 μL of Calibration Stock 1, 50 μL of Calibration Stock 2, and 500 μL of Calibration Stock 3 to the tube and dilute to 50 mL with reagent water.
7.11.4 Calibration Standard 3: 100 μg/L of Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Tl, Th, U, V, and Zn; and 10mg/L Na, Ca, Mg, K, and Fe. Fill a 50-mL autosampler tube with approximately 20 mL of reagent water. Add 1 mL of 1:1 nitric acid. Pipette 250 μL of Calibration Stock 1, 250 μL of Calibration Stock 2, and 5000 μL of Calibration Stock 3 to the tube and dilute to 50 mL with reagent water.

Note: *Remember to spike all solutions with 100 μL of the internal standard stock solution.*

7.12 ICV Standard: Prepare fresh daily or as needed for analysis. The following concentrations are suggested when the standards in Section 6.10 are used: 50 μg/L of Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Tl, Th, U, V, and Zn; and 5mg/L Na, Ca, Mg, K, and Fe. Fill a 50-mL autosampler tube with approximately 20 mL of reagent water. Add 1 mL of 1:1 nitric acid. Pipette 250 μL of ICV Stock 1, 250 μL of ICV Stock 2, and 2500 μL of ICV Stock 3 to the tube and dilute to 50 mL with reagent water.

7.13 Dual Detector Cross-Calibration Solution: contains 250 µg/L each of Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Tl, Th, U, V, Zn, Na, Ca, Mg, K, Fe, Sc, Y, In, Rh, Tb, Ho, and Bi and 1250 µg/L Ge. Prepare by adding 1.25 mL of Calibration Stock 1, 1.25 mL of Calibration Stock 2, 125 µL of Calibration Stock 3, and 1.25 mL of the Internal Standard Stock Solution (from 6.9) to a 50-mL autosampler tube containing 25 mL reagent water and 1 mL 1:1 nitric acid. Dilute to 50 mL with reagent water and mix well.

> ***Note:*** *You should also add comparable concentrations of any interfering elements or species, such as chloride, whose intensities may be used in interference corrections to ensure correct equations if the measured intensities are in the analog range of the detector. For example, if the EPA SW-846 3050 digestion is to be measured at a 1:10 dilution, resulting in an hydrochloric acid concentration of 0.5%, the detector cross calibration solution should be made in 0.5% hydrochloric acid.*

7.14 Interference Check Solution Stock 1: Contains 1000 mg/L each of Al, Ca, Fe, Mg, Na, P, K, and S; 2000 mg/L of C; 10,000 mg/L Cl, and 20 mg/L each of Mo and Ti.

> ***Note:*** *It is suggested that this solution be purchased from a standards vendor providing high quality solutions for ICP-MS.*

7.15 Interference Check Solution Stock 2: Contains 10 mg/L each of As, Cd, Cr, Co, Cu, Mn, Ni, Ag, and Zn.

> ***Note:*** *It is suggested that this solution be purchased from a standards vendor providing high quality solutions for ICP-MS.*

7.16 Interference Check Solution A (ICSA): Contains 100 mg/L each of Al, Ca, Fe, Mg, Na, P, K, and S; 200 mg/L of C; 1000 mg/L Cl, and 2 mg/L each of Mo and Ti.

7.16.1 Prepare by diluting the Interference Check Solution Stock 1 tenfold with reagent water Pipette 5 mL of ICS Stock 1 into a 50 mL autosampler tube, dilute to 50 mL with reagent water.

7.16.2 Add internal standards at the levels present in all blanks, standards, and samples.

7.16.3 Prepare this solution fresh daily.

7.17 Interference Check Solution AB (ICSAB): Contains 100 mg/L each of Al, Ca, Fe, Mg, Na, P, K, and S; 200 mg/L of C; 1000 mg/L Cl, 2 mg/L each of Mo and Ti, and 0.020 mg/L each of As, Cd, Cr, Co, Cu, Mn, Ni, Ag, and Zn.

7.17.1 Prepare by diluting the Interference Check Solution Stock 1 tenfold with reagent water Pipette 5 mL of ICS Stock 1 into a 50 mL autosampler tube.

7.17.2 Add 100 µL of Interference Check Solution Stock 2 into the tube, dilute to 50 mL with reagent water.

7.17.3 Add internal standards at the levels present in all blanks, standards, and samples.

7.17.4 Prepare this solution fresh daily.

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time
Waters	HDPE	50 mL	HNO_3, pH < 2	180 Days
Soils	Plastic or Glass	3 g	None	180 Days

9.0 QUALITY CONTROL

9.1 Initial Demonstration of Capability

A summary of quality control requirements including type, frequency, acceptance criteria and corrective action is maintained in the LIMS. Prior to analysis of any analyte the following requirements must be met.

9.1.1. Instrument Detection Limit (IDL). IDLs can be determined by calculating the average of the standard deviations of the three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. Each measurement must be performed as a separate analytical sample. The IDL should be performed every three months. The IDL is calculated by multiplying by 3, the average of the standard deviations obtained on three nonconsecutive days.

9.1.2. Linear Calibration Ranges - Linear calibration ranges are primarily detector limited. The linear range must be determined at instrument setup, and the upper limit must be verified annually or whenever a change in instrument hardware or operating conditions, in the judgment of the analyst, may lower expected ranges. Standards used to determine or verify linear ranges must be analyzed during a routine analytical run. The linear range is the concentration above which sample results cannot be reported.

9.1.2.1. For initial determination of the upper limit of the linear range, determine the signal responses from three different concentration standards across the estimated range. One standard must be at the upper limit of the estimated range. Results must recover within 10% of the expected value for the three standards. The Linear Range is then set at the concentration of the high standard.

9.1.2.2. For verification of the upper limit of the linear range, the high standard must recover within 10% of its expected value

9.1.3. Method Detection Limit (MDL) - The laboratory shall determine a method detection limit for all analytes of interest initially and annually thereafter. The MDL study is performed and calculated according 40CFR Part 136 Appendix B.

9.2. A batch is a group of no greater than 20 samples excluding QC samples (LCS, Method Blank, MS, MSD) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24 hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.3. One method blank (MB) must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit (exception: common laboratory contaminants, see below) or at or above 5% of the measured concentration of that analyte in associated samples, whichever is higher (sample result must be a minimum of 20x higher than the blank contamination level).

9.3.1. If the analyte is a common laboratory contaminant (copper, iron, lead, calcium, magnesium, potassium, sodium or zinc) the data may be reported with qualifiers if the concentration of the analyte in the method blank is less than two times the RL. Barium, Chromium and Manganese may also be considered common laboratory contaminants at ICPMS reporting limits. **Such action must be addressed in the narrative.**

9.3.2. Re-preparation and re-analysis of all samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples (see exception noted above).

9.3.3. If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported. **Such action must be addressed in the narrative.**

9.3.4. If the above criteria are not met and re-analysis is not possible, then the sample data must be qualified. **This anomaly must be addressed in the narrative.**

9.3.5 For dissolved metals samples which have not been digested, a CCB result is reported as the method blank. The CCB run immediately prior to the start of the dissolved sample analyses must be used for this purpose. No more than 20 samples can be associated with one CCB

9.4. Laboratory Control Sample (LCS)

9.4.1. One LCS must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. The historical limits for the LCS for each analyte are in the LIMS. If the LCS exceeds these limits for any analyte, that analyte is judged to be out of control and must be corrected before the analysis can be reported.

9.4.2. Corrective Action for LCS

9.4.2.1. If any analyte is outside established control limits the system is out of control and corrective action must occur.

9.4.2.2. The only exception is that if the LCS recoveries are biased high and the associated sample is ND for the parameter(s) of interest, the batch is acceptable. **This must be addressed in the narrative.**

9.4.2.3. Corrective action will be re-preparation and re-analysis of the batch unless the client agrees that other corrective action is acceptable.

9.5. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.5.1. One MS/MSD pair must be processed for each batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results apply only to the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis. The historical spike recovery acceptance limits for each analyte are in the LIMS. If they are not in control and all other quality control criteria have been met, then a matrix interference is suspected.

9.5.2. Corrective action for MS/MSDs

9.5.2.1. If the analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include re-preparation and re-analysis of the batch.

9.5.2.2. If the native analyte concentration in the MS/MSD exceeds 4x the spike level for that analyte, the recovery data is flagged as not applicable.

9.6. Sample Duplicate

9.6.1. A sample duplicate (DUP) is a second aliquot of an environmental sample, taken from the same sample container that is processed with the first aliquot of that sample. The sample and DUP results are compared to determine the effect of the sample matrix on the precision of the analytical process. As with the MS/MSD results, the sample/DUP precision results apply only to the specific sample, and not to other samples in the batch.

9.6.2. Sample duplicates may be performed in lieu of or in addition to MSDs when there is a high expectation of sample concentrations above the .

9.7. Control Limits

9.7.1. Control limits are established by the laboratory as described in the Quality Assurance Manual.

9.7.2. Laboratory control limits are internally generated and updated periodically unless method specified.

9.8. MDLs and MDL Checks are established by the laboratory as described in the Quality Assurance Manual.

9.9. ICV/CCV - Calibration accuracy is verified at the beginning of each analytical run by analyzing a second-source initial calibration verification (ICV) standard. A continuing calibration verification (CCV) standard is analyzed at a 10% frequency throughout the run. The ICV must be within 10% of the expected value, or the analysis is terminated. The CCV must be within 10% of the expected value for method 6020A or 15% of the expected value for method 200.8. Sample results may only be reported when bracketed by valid CCV's.

9.10. Lower Limit of Quantitation Check (LLQC) should be analyzed after establishing the lower laboratory reporting limits and on an as needed basis to demonstrate the desired detection capability. LLQCs are verified when all analytes in the LLQC are detected within 30% of their true value. This check should be analyzed analyzed after the ICV and at the end of each analytical batch. A more frequent LLQC may be needed (i.e., every 10 samples) if low level sample concentrations are anticipated and the system stability at the low end is questionable.

9.11. ICB/CCB/CB - The initial calibration blank must be analyzed immediately following the ICV. The continuing calibration blank must be analyzed at a frequency of 10% throughout the remainder of the analytical run. The ICB/CCB must fall within +/- the reporting limit from zero.

9.12. Interference Check Solutions (ICSA/ICSAB) ***Method 6020 only***- The interference check solution is prepared with known concentrations of interfering elements so a determination may be made as to the magnitude of the interference on analytes of interest as well as a test of any software corrections. The required elements and their concentrations are listed in Table V. The interference check solutions must be analyzed at the beginning of every analytical run and every 12 hours thereafter. The results of solution "A" and solution "AB" should be monitored for possible interferences.

9.12.1. Control limits of spiked analytes in the ICSA/ICSAB solution are +/- 50% of true value. Control limits of non-spiked analytes are +/- 2x the reporting limit or less than 1 ug/L.

> ***Note***: *It may not be possible to obtain absolutely clean ICSA/ICSAB standards. If contamination can be confirmed by another method (ICP/GFAA), acceptance criteria will be applied at that level and the data accepted.*

9.13. Internal Standards – The intensities of all internal standards must be monitored throughout the run. The internal standard in the samples must be greater than 70% of the intensity of the internal standard in the initial calibration standard for Method 6020A, and between 60% and 125% for Method 200.8. If the sample falls outside of these criteria, perform the following procedures. First, evaluate nearby CCVs and CCBs. If sample internal standard recoveries appear to be related to instrument drift, then rerun affected samples. If sample internal standard recoveries appear to be primarily sample or matrix related, then perform appropriate dilutions until the internal standard recoveries are within the method criteria. The sample must be diluted fivefold (1:4) and reanalyzed with the addition of appropriate amounts of internal standards. If the first dilution does not eliminate the problem, this procedure must be repeated until the internal standard intensities rise to a minimum 70% limit. Reported results must be corrected for all dilutions. Alternately, the run may be reprocessed with an alternative internal standard that is not in the samples and at an appropriate mass for the masses being reported.

9.14. Serial Dilution ***Method 6020 only*** - One serial five-fold dilution should be analyzed per batch for each matrix. If the analyte concentration is within linear range of the instrument and sufficiently high (generally, a factor of 100 times above the reporting limit), the serial dilution must agree within 10% of the original analysis. If not, an interference effect must be suspected, the result is flagged and included in the final report narrative. Samples identified as blanks cannot be used for serial dilution.

9.15. Post-Digestion Spike Addition (PDS) ***Method 6020 only*** - If the serial dilution and or matrix spike fails to meet the acceptance criteria, a PDS should be performed as follows. An analytical spike is added to a portion of a prepared sample, or its dilution, and should be recovered within 80- 120% of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the lower limit of quantitation. If the PDS fails to meet this criterion, matrix interference should be suspected.

10.0 PROCEDURE

10.1 Sample Preparation – Preliminary acid digestion is required for groundwater, aqueous samples, sludges, sediments, and other solid wastes for which total (acid- leachable) elements are requested. See prep SOPs for preparation details.

10.2 Calibration

Set up the instrument according to manufacturers operating instructions. Allow the instrument to become thermally stable for at least 30 minutes before tuning. The concentrations of the standards used should be entered into the calibration page of the analytical method in the ELAN software according to the values of the standards prepared in Section 6.10.

- 10.2.1 Linear Through Zero curve type should be selected for all analytes.
- 10.2.2 The calibration blank will be run as a blank, before the analysis of any actual calibration standards.
- 10.2.3 The first standard run should be the lowest level standard containing analyte, followed by standards of increasing concentration in order to minimize cross-contamination and carryover.

10.3 Initiate the plasma and allow a warm-up of at least 30 minutes. The tuning procedures may be carried out during warm-up.

10.4 Open the EPA200 TUNE method and optimize the following parameters using the 10 ppb tuning solution containing Be, Mg, Co, Rh, In, Ba, Ce, and Pb.

- 10.4.1 Set RF power to desired level
  - 10.4.1.1 1000-1100 watts for clean waters
  - 10.4.1.2 1400 watts for soil and sediment digests
- 10.4.2 Optimize the nebulizer argon flow
- 10.4.3 Optimize the static lens voltage
- 10.4.4 Save the Optimization file

10.5 Open the EPA200 LENS CALIB method and perform the autoLens calibration using the 10 ppb 200.8 tuning solution.

- 10.5.1 Clear the old calibration
- 10.5.2 Click on Get Analytes
- 10.5.3 Click on Optimize (the procedure takes about 6 minutes)

10.6 Save the Optimization File

10.7 Open the EPA200 DETECTOR CALIB method and aspirate the dual detector calibration solution (250-500 ppb solution containing all elements to be quantitated plus the internal standard elements and any elements used for interference correction, such as Cl).

> ***Note:*** *This procedure is only required when detector voltages are changed or a new detector is installed.*

- 10.7.1 Run the detector cross calibration routine
  - 10.7.1.1 Clear the old calibration
  - 10.7.1.2 Click on Get Analytes
  - 10.7.1.3 Click on Optimize
- 10.7.2 Save the Optimization File
- 10.7.3 Print out the Optimization File (if desired).

10.8 Open the EPA200 TUNE method

- 10.8.1 Aspirate the 10 ppb 200.8 Tuning solution
- 10.8.2 Click on the Calibrate button in the Tuning window
- 10.8.3 Check that the resolution at Mg 24 and Pb 208 is less than or equal to 0.65 amu (measured at 10% peak height)

> ***Note:*** *It has been shown that 0.65 amu at 10% peak height is equivalent to 0.75 amu peak height at 5% peak height.*

10.8.4 Check mass calibration, save the new calibration if the measured mass is greater than 0.1 amu from the true mass.
10.8.5 Print the tuning window using Paint, if documentation is required.

Note: *Using the Clock feature in Windows a data/time stamp can be added to the printout by dragging the clock onto the tuning window.*

10.9 Open the EPA200 DAILY method.
10.9.1 Aspirate the 10 ppb 200.8 tuning solution
10.9.2 Click on the Analyze button in manual sample window to acquire
10.9.3 Check that the RSDs for the five replicates for all Be, Mg, Co, In, Rh, and Pb are all less than 5%.
10.9.4 Monitor daily performance measures as recommended by Perkin Elmer of Rh sensitivity, background, % double charged and % oxide levels.
10.9.4.1 Rh > 150,000 cps for 10 ppb
10.9.4.2 Background at mass 220 < 30 cps
10.9.4.3 % double charged < 3%
10.9.4.4 % oxides < 3%

Note: *Oxides and double charged levels can be reduced by slightly decreasing the nebulizer flow rate.*

10.10 Open the EPA200 method.
10.11 Prepare calibration standards.
10.12 Make any desired changes to the method and save method under a different name. (The EPA200.mth method is write protected.)
10.12.1 Load the calibration blank and calibration standards into the autosampler positions specified in the autosampler page of the analytical method.
10.12.2 Load the Quality Control samples defined in the QC checking part of the method into the autosampler according to the positions entered in the QC Autosampler page of the method. (See the QC Manual for more information on setting up Quality Control Protocols.)
10.13 Edit the Sample window for batch analysis to update with new sample information.

Note: *Only enter sample, QC spike, QC duplicate, QC dilution, or reagent blank information in the batch sample page. Calibration standards and QC standards are defined in the relevant sections of the Method.*

10.13.1 Load the applicable method for the sample batch.

Note: *If automatic QC checking is used the method must be the same for all samples.*

10.13.2 The Calibration action for the first sample for which concentration results are desired must be "analyze blank, standards, and sample"
10.13.3 The calibration action for all other samples is usually "Analyze Sample", unless periodic recalibration is desired.
10.13.4 Enter peri-pump control speeds for all samples
10.13.5 Save Sample file
10.13.6 Re-Open the sample file (this must be done for the batch QC to run properly)
10.13.7 Load the samples into the autosampler positions specified in the Sample file.
10.13.8 Select the samples to be analyzed by highlighting the row number with the mouse
10.13.9 Select "Analyze Batch". Aspirate the rinse blank for 5-10 minutes before beginning a batch run to avoid carry-over and contamination.

10.14 Sample Analysis – Flush the system with the rinse blank for at least 30 seconds between samples and standards during the analytical run.

10.14.1 Masses which would affect the data quality must be monitored during the analytical run to determine the potential effects of matrix on a given element.

10.14.2 Dilute and reanalyze samples that are more concentrated than the linear range for an analyte or specific isotope of interest. No analyte may be reported from an analysis of a diluted sample in which the analyte concentration is less than 5 times the IDL (the sample should be diluted to the approximate midrange of the analytical curve), unless the dilution is for internal standard recoveries.

10.14.3 The analytical run sequence should be performed as follows to meet all quality control criteria:

Analytical Sequence

Warm-up	ICSA (6020 Only)
Verify instrument performance	ICSAB (6020 Only)
Calibration blank	CCV
Calibration standards	CCB
ICV	10 Samples*
ICB	CCV*
RL verification standard	CCB*

* - Repeat as needed with additional samples

10.15 Analytical Documentation

10.15.1 Record all analytical information in the analytical logbook/logsheet, which may be in an electronic format, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method.

10.15.2 All standards are logged into the LIMS. All standards are assigned a unique number for identification by the LIMS.

10.15.3 Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

10.15.4 Sample results and associated QC are entered into the LIMS after final technical review.

11.0 CALCULATIONS / DATA REDUCTION

11.1 See Section 25, TestAmerica Watertown Quality Assurance Manual.

12.0 METHOD PERFORMANCE

12.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.
12.2 Current MDLs and LOQs for this method are maintained in the LIMS for reporting purposes.
12.3 This method was initially validated by TestAmerica on 01/29/08. That data is available on file.

13.0 POLLUTION CONTROL

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability).

14.0 WASTE MANAGEMENT

14.1 All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."
14.2. Solid materials (gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.
14.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of TestAmerica. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by an annual refresher training.
14.4. Acid waste consisting of sample and rinse solution is generated by this method. Aqueous waste can be poured down the drain if the pH is between 4 and 10. Any sample waste generated that is not in this pH range must be pH adjusted to a pH between 4 and 10 prior to disposal.

15.0 REFERENCES / CROSS-REFERENCES

15.1 Quality Manual – TestAmerica Watertown
15.2 SOP CW-Q-S-002 – Writing a Standard Operating Procedure (SOP)
15.3 SOP WT03-07 – Sample Preparation for Metals Analysis by FLAA and ICP-AES
15.4 SOP WT07-02 – Waste Disposal

16.0 METHOD MODIFICATIONS

Item	Method	Modification
Standards	200.8 and 6020A	Commercially available standards are purchased and verified at the laboratory rather than being prepared from the solid material. These verification records are kept in the laboratory.
Calibration blank	200.8 and 6020A	The results of the calibration blank as well as all other blanks must be less than the reporting limit, not 3 times the instrument IDL
Reagent water	200.8 and 6020A	ESS Ultra Pure blank water is substituted when reagent water is called for. This water is tested to be free of contaminants by the analysis of blanks, and is certified as >18 megOhm-cm.
Resolution criteria	200.8	Resolution criteria of the mass calibration is met if the resolution criteria for method 6020A is satisfied

17.0 ATTACHMENTS

17.1 The following are the flags that could routinely be expected to be used for this analysis. The usages that are listed are not meant to be all-inclusive, they are only to serve as examples.

Qualifier	Description
B	Analyte was detected in the associated Method Blank.
B1	Analyte concentration in the sample is greater than 20x the concentration found in the method blank. This blank result meets regulatory acceptance criteria.
J	Results reported between the Method Detection Limit (MDL) and Limit of Quantitation (LOQ) are less certain than results at or above the LOQ.
L1	Laboratory Control Sample and/or Laboratory Control Sample Duplicate recovery was above acceptance limits.
L2	Laboratory Control Sample and/or Laboratory Control Sample Duplicate recovery was below acceptance limits.
M*	Spike recovery limits are not applicable when the sample concentration is greater than or equal to 4 times the spike added. The LCS or CCV analyzed concurrently with these samples met control criteria.
M1	The MS and/or MSD were above the acceptance limits due to sample matrix interference. See Blank Spike (LCS).
M2	The MS and/or MSD were below the acceptance limits due to sample matrix interference. See Blank Spike (LCS).
MHA	Due to high levels of analyte in the sample, the MS/MSD calculation does not provide useful spike recovery information.
N1	See case narrative.
P	The sample, as received, was not preserved in accordance to the referenced analytical method.
P2	Sample received without chemical preservation, but preserved by the laboratory.
P7	Sample filtered in lab.
RL1	Reporting limit raised due to sample matrix effects.
S6	Sediment present.

17.2 Any deviations from this SOP must be documented and brought to the attention of the appropriate Operations Manager, the Laboratory Director, or the QA Manager.

18.0 REVISION HISTORY

- Revision 0, dated 01/28/08
  - New SOP Format and Title.